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REACTION BETWEEN COPPER REVERBERATORY SLAG AND REFRACTORIES*

By Sahap S. Kocatopcu†

Abstract

Small slag cylinders placed on top of different refractory brick were heated at 1300° and 1400°C. Depth and width of reaction and diffusion zones were measured, and thin sections through the penetrations were studied.

I. Introduction

The copper reverberatory furnace is mainly used for melting the ore concentrate to form a suitable matte and to separate the matte from other impurities. Since in a reverberatory furnace the heat is primarily transmitted by radiation and since the latter varies with the fourth power of the absolute temperature, there is a continuous tendency toward increasing the temperature for higher efficiencies. The available refractories, however, set a limit to a higher temperature, which has the effect of lowering their softening point and accelerating their corrosion. This corrosion, in the case of copper reverberatory furnaces, is also caused by the variations of the slag level. The same section of the wall is exposed successively to the attack of the gas and dust, to the slag, and to the matte at different working conditions.

Thus, the study of the behavior of refractories in this furnace is rather complicated. To accomplish this study, those properties of the brick must be investigated which are affected in the furnace and which can also be studied in laboratory experiments. Physical properties, such as melting and softening points, texture, tensile strength, resistance to abrasion, thermal conductivity and emissivity, and the chemical properties which can be investigated by macroscopic, petrographic, analytical, and X-ray examinations can be subjected to laboratory measurements, and the results can be interpreted in view of brick performance in smelting plant practice.

The purpose of this paper is to give data on the slag resistance of the copper reverberatory refractories.

II. Review of Literature

Although the reactions between refractories and slags of iron, steel, and glass have been the subject of many investigations, little has been published concerning similar reactions in copper slag.

In the literature dealing with copper metallurgy, Oldright and Schroeder[1] suggest that higher temperatures in the hot zone of the reverberatory furnace be used and that a refractory of better quality is necessary before these temperatures can be increased much further.

Boericke[2] stresses the importance of laboratory research on refractories and gives some thin-section pictures of brick to be used in copper smelting.

Suydam[3] gives a good picture of the historical development of the refractories used in the copper industry. Starting from the fire-clay brick, he stresses the fact that the use of magnesite or chrome-magnesite brick is the last step in the evolution.[3] "Trials of high melting-point refractories indicate none of more promise than magnesite. In a test conducted at the El Paso plant of the American Smelting and Refining Company at and above the slag line, high-alumina brick were the first to fail when tested in panels along with chrome brick, first-quality fire-clay brick, magnesite brick, and silica brick. Petrographic examination* of the fused surface disclosed the reason to be the formation of complex aluminum silicates with the constituents of the furnace dust. Silicon carbide brick, while a splendid refractory in many services, failed in a similar panel test at Tacoma owing to the fluxing action of basic oxides of the furnace dust. Brick, made in Har-

* Presented at the Forty-Sixth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 5, 1944 (Refractories Division). Received May 22, 1944; revised paper received December 13, 1944.

Prepared from material in a thesis submitted in partial fulfillment of the requirements for the degree of Master of Science, Massachusetts Institute of Technology, Cambridge, Mass.

† Research Assistant, Dept. of Metallurgy, Massachusetts Institute of Technology.

[1] G. L. Oldright and F. W. Schroeder, "Smelting Copper in the Reverberatory Furnace," *Trans. Amer. Inst. Mining Met. Engrs.*, **76**, 461 (1928).

[2] W. F. Boericke, "Methods of Research Newly Applied to Refractories," *Mining and Met.*, **10** [265] 16–18 (1929); *Ceram. Abs.*, **8** [3] 193 (1929).

[3] A. G. Suydam, "Application of Refractories to the Copper Industry," *Trans. Amer. Inst. Mining Met. Engrs.*, **106**, 262–77 (1933); p. 266.

* Personal communication of R. D. McLellan, Perth Amboy, N. J., to A. G. Suydam.

bison-Walker Refractories Company laboratories, containing high percentages of mullite, while showing remarkable strength at high temperatures, failed to resist the fluxing action as well as did first-quality, fireclay brick."

Heuer[4] stresses the importance of teamwork between refractory manufacture and smelter operation; he also indicates the use of different types of magnesite and chrome-magnesite brick in the copper smelter. Seil[5] and Heuer[6] describe the manufacture of chrome and chrome-magnesite brick fabricated both in burned and chemically bonded form.

In the recent article analyzing the modern copper smelting, Wagstaff[7] points out that the increase of tonnage smelted per furnace-day has made the problem of furnace life very important. He also indicates that the use of water-cooled jackets along the bath line of deep-bath smelting furnaces is becoming a standard practice.

Every known type of refractory, acid, basic, and neutral, has been tried, with little or no success. When furnace tonnages are stepped up above 1200 tons per furnace-day, the cost of side-wall repairs becomes a very important item. In most plants, copper jackets with $1^1/_2$-in. water coils have proved most satisfactory.

This review of the literature shows that there is not much published information on the reaction between copper slag and refractories. One of the best published investigations on the action of slags is by Hugill and Green[8]; although it deals with iron blast-furnace slags, the data were obtained from three different tests.

The first test is essentially a determination of the refractoriness of mixtures of varying proportions of finely ground brick and slag. It was first used by Mellor[9] and was later developed by Howe, Phelps, and Ferguson.[10]

The second test is the one adopted in the present investigation and consists of melting a slag cylinder on the surface of the brick. It may be taken to indicate some index of the corrosive action of the slag on a particular refractory. "In addition to the chemical reactions involved, the results are also dependent on the texture of the surface and body of the brick. Some tests of similar nature have been previously designed by Miehr, Kratzert, and Immke,[11] who used holes bored into the brick as receptacles for the slag. Salmang and co-workers[12] used a specially constructed crucible. The Refractory Materials Standardization Committee[13] suggested a ring cemented to the surface of the brick as a container for the slag. The method adopted in this investigation was preferred to those just mentioned because, when holes are bored or when a ring is cemented on the brick, the skin of the brick is altered before the test is started."*

The third test was carried out to obtain some sign of erosive action of slags on brick at working temperatures. It was designed first by Mellor and Emery[14] and consists in feeding the slag into the air-blast stream, the slag thus being carried forward to the brick which is vertically placed in a furnace.

III. Materials and Apparatus

The slag, obtained through the courtesy of one of the western copper smelters, was of the following percentage analysis: Insoluble† 39.3, Fe 33.7, CaO 7.1, Al_2O_3 5.2, Cu 0.37, and Ag 0.035.

Assuming that the insoluble content is completely silica and that iron is in the form of ferrous oxide (FeO) during smelting, and neglecting the minor constituents such as copper and silver, the percentage composition can be evaluated as follows: SiO_2 41.7, FeO 45.2, CaO 7.6, and Al_2O_3 5.5.

The acidity or basicity of a slag may be determined by the ratio of oxygen molecules in acid oxides to the oxygen molecules in basic oxides. The alumina, although neutral in general, may act acid or basic in order to neutralize the high acidity or basicity of the slag; in the present case, it would act as a basic oxide. The acidity calculated with these assumptions is 1.8. Thus the slag is fairly acid, and the alumina, wherever in contact with it, will tend to neutralize it by forming lower melting eutectics.

The refractories used are summarized in Table I.

The furnace in which the reaction was performed was a Globar electric furnace, 1.5 foot square in cross-section area. The eight heating elements were equally distributed on two opposite walls. These Globars were the new type, and no water cooling was necessary during the heating. A silicon carbide slab was put into the bottom of the furnace in order to equalize the temperature distribution and to prevent eventual corrosion of the furnace bottom. A platinum, platinum-rhodium

[4] R. P. Heuer, "Refractories," *Trans. Amer. Inst. Mining Met. Engrs.*, **106**, 278–81 (1933); *Ceram. Abs.*, **14** [5] 118 (1935).

[5] G. E. Seil, "Refractories from Metallurgical Viewpoint," *Ind. Heating*, **2** [9] 517–21, 538–40 (1935); *Ceram. Abs.*, **15** [3] 94 (1936).

[6] R. P. Heuer, "New Application of Ritex Process to the Manufacture of Chrome Brick," *Steel*, **97**, 22–25, 30 (August 19, 1935); *Ceram. Abs.*, **15** [5] 151 (1936).

[7] R. A. Wagstaff, "Changes and Improvements in Modern Copper Smelting," *Amer. Inst. Mining Met. Engrs., Tech. Paper*, No. 1669; *Metals Tech.*, **11** [2] 9 pp. (Feb., 1944); p. 5.

[8] W. Hugill and A. T. Green, "Action of Slags on Refractory Materials: I, Application of Certain Tests to Study of Action of Blast-Furnace Slags on Refractory Materials," *Iron & Steel Inst., Special Rept.*, No. 26, pp. 295–349 (1939).

[9] J. W. Mellor, "Action of Flue Dust on Firebrick," *Trans. Ceram. Soc.* [England], **13**, 12–14 (1914).

[10] R. M. Howe, S. M. Phelps, and R. F. Ferguson, "Action of Slag on Silica, Magnesite, Chrome, Diaspore, and Fire-Clay Refractories," *Jour. Amer. Ceram. Soc.*, **6** [4] 589–95 (1923).

[11] W. Miehr, I. Kratzert, and H. Immke, "Beitrag zur Bestimmung der Schlackenwieder-standfähigkeit feuerfester Baustoffe," *Tonind.-Ztg.*, **51**, 121–22 (1927); *Ceram. Abs.*, **6** [10] 449 (1927).

[12] Hermann Salmang and co-workers, "Untersuchungen über die Verschlackung feuerfester Stoffe," *Stahl u. Eisen*, **47** [43] 1816–20 (1927); **50** [52] 1814 (1930); *Ceram. Abs.*, **7** [2] 85 (1928); **10** [5] 353 (1931).

[13] Refractory Materials Standardization Committee, "Standardization of Tests for Refractory Materials, III," *Trans. Ceram. Soc.* [England], **18**, 516–17 (1918).

[14] J. W. Mellor and W. Emery, "Corrosive Action of Flue Dust on Firebrick," *ibid.*, **18**, 230–50 (1918).

* For citation, see Hugill and Green, footnote 8, p. 296.

† Insoluble in hydrochloric and nitric acids.

TABLE I
SUMMARY OF REFRACTORIES USED AND RESULTS*

Brick No.	Type	Porosity (%)	Remarks	Temp. (°C.) 1300	1400	1300	1400	1300	1400	1300	1400	1300	1400
				AB (mm.)		*AC* + *BD* (mm.)/2		*EF* (mm.)		*EG* (mm.)		*EH* (mm.)	
1	Silica	26		58	64	13	15	4	7	15	31	Negligible	Nil
2	Fire clay		Moderate heat duty	80		Negligible		Negligible		1	1	2	"
3	Fire clay	18	Superduty, 44% Al_2O_3	86	100	"		Negligible	8	1	1	2	"
4	Fire clay	13	Superduty, 45.5% Al_2O_3	62	102	"		"	3	1	1	5	"
5	Fire clay	12	Superduty, 45.5% Al_2O_3	72	106	"		"	4	1	1	3	1
6	Alumina	21	50% Al_2O_3	71	82	Negligible	13	"	3	1	1	4	Nil
7	Alumina	24	70% Al_2O_3	60	78	"	17	1	7	3	2	5	"
8	Magnesite	22	82–85% MgO, molded under heavy pressure, and fired at very high temp.	50	64	10	14	1	2	4	2	3	1
9	Forsterite	25	Negligible shrinkage at 1650°C. reheat	50	54	12	16	2	6	13	18	2	2
10	Chromite	21	Solely blend of ground chrome ores, molded under heavy pressure and burned at very high temp..	63	62	4	5	1	1	9	12	3	2

* *AB*, avg. diameter of molten slag section; *AC* + *BD*/2, avg. width of diffusion zone; *EF*, depth of reaction zone; *EG*, depth of penetration; *EH*, height of slag layer.

thermocouple was introduced into the furnace through a hole from the roof, and the end of it was kept at 1 in. distance from the reaction surface.

IV. Summary of Work

The previously mentioned slag, passing through a 200-mesh screen, was mixed with 6% water and 2% dextrine to form small cylinders, $1^3/_8$ in. in diameter and $^3/_4$ in. high. From the ten refractory brick (Table I), pieces were cut, $4^1/_2$ by $4^1/_2$ by $2^1/_2$ in. in size. These pieces were placed, six in a batch, in the large Globar electric furnace. On the top of each brick piece, a slag sample was placed (Fig. 1). This

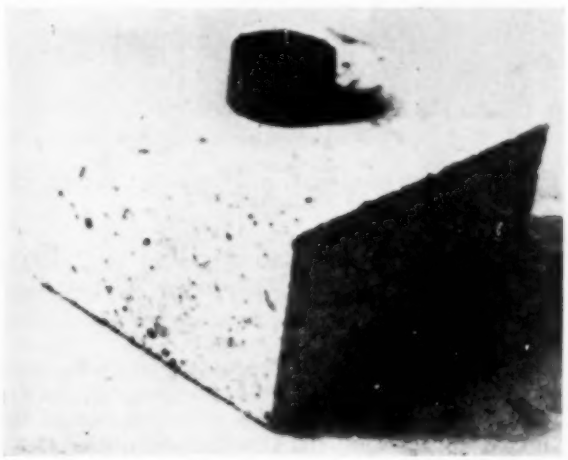

FIG. 1.—Slag sample on refractory specimen to be tested.

set was then heated up to 1300°C., and this temperature was maintained for six hours. After slow cooling, the brick were cut in vertical cross sections in order to study the corrosion. The same procedure was repeated by heating another set up to 1400°C., held constant for 24 hours. The thin sections made through cross sections of the 1300°C. run showed clearly the slag-reaction and diffusion zones as distinct from the unattacked brick body. These studies in many cases resulted in a satisfactory explanation of reaction mechanism. In the magnesite brick, X-ray powder diffraction patterns were obtained in order to have complementary data on the crystal structure of the components formed at the reaction zone.

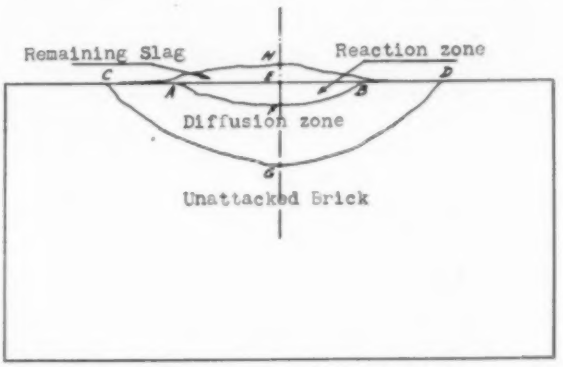

FIG. 2.—Vertical cross section of fired brick showing different zones.

V. Results

The macroscopic study of the vertical sections of the attacked brick usually revealed two layers, which may be called reaction zone and diffusion zone, respectively. Below this was the unattacked brick. The various measurements made can be better explained by referring to Fig. 2. The average diameter of the molten slag layer is given by *AB;* the average width of the diffusion zone by $\frac{AC + BD}{2}$; the depth of reaction zone by *EF;* the depth of penetration by *EG;* and the height of the slag layer by *EH*. The details of the results are given in Table I and illustrated by Figs. 3 to 12.

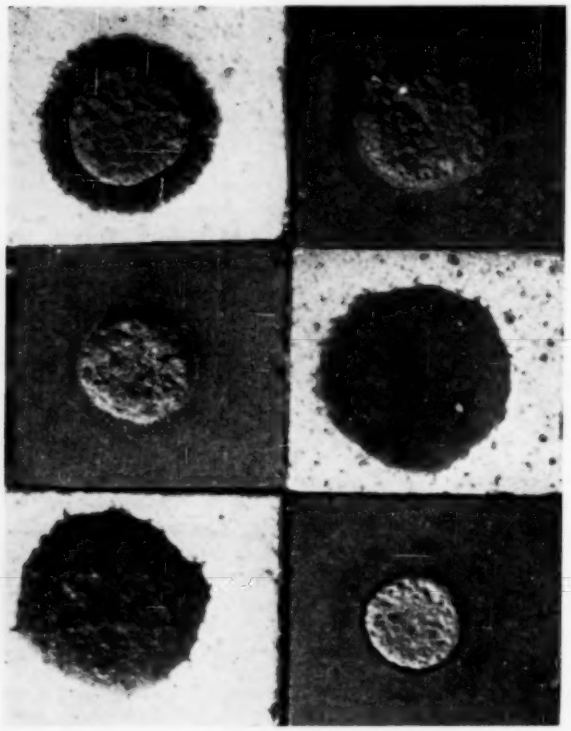

Fig. 3.—Set of brick taken from furnace after 1300°C. run; left row, top to bottom, brick Nos. 1, 9, and 2; right row, top to bottom, brick Nos. 10, 3, and 8.

The microscopical studies were made on the thin sections, and the pictures taken at high magnifications illustrate the history of the slag action.

(1) Silica Brick

The silica brick shows the deepest penetration, particularly the one of the 1400°C. run, in which case all of the slag is absorbed by the brick. The penetration is red at the reaction zone, becomes bluish-brown in the diffusion zone, and lighter in color near the unattacked part. The large ganister grains preserve their shape; they are colored by the slag which penetrates them by zone; and an unattacked silica portion sometimes is left at the center of the grains.

The deep penetration of the slag is primarily due to the high porosity of the brick. The acidic character of the slag diminishes the very corrosive action of basic oxides, especially that of ferrous oxide. A study of the ternary diagram SiO_2–FeO–CaO, the latter including the alumina, gives about 1120°C. for the melting point of the slag, but when this slag gets in contact with the silica, the melting point of the eutectic is rather high.

The thin-section studies show that most of the silica grains are in the form of cristobalite and tridymite, the large grains occasionally containing small quartz inclusions. In the attacked and unattacked portions of the thin section, these silica grains have their periphery darkened by a thin layer of minute cristobalite crystals. This layer is further darkened in the attacked zone because of slag action. Upon cooling from 1300°C., the remaining slag on top of the brick is separated from the body in the form of a thin crust.

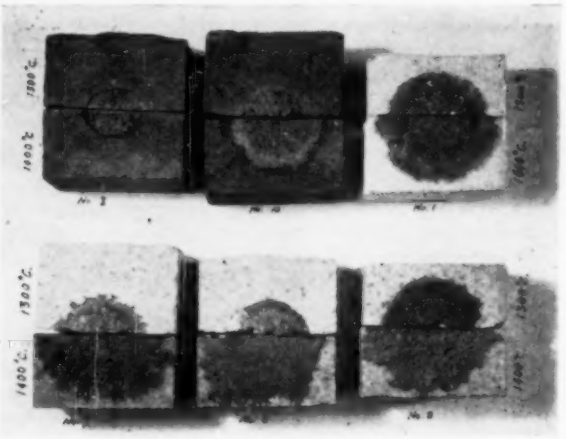

Fig. 4.—Top view of different brick after runs of 1300°C. and 1400°C., respectively.

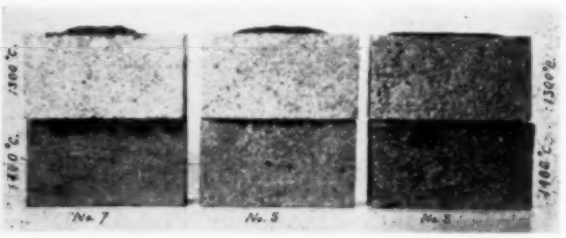

Fig. 5.—Vertical cross sections of fire-clay and alumina brick.

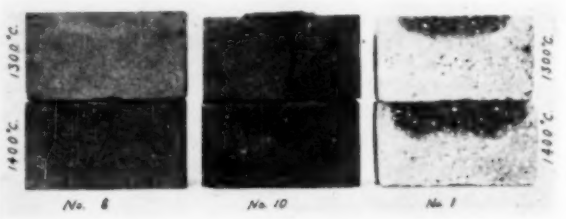

Fig. 6.—Vertical cross sections of forsterite, chromite, and silica brick.

(2) Fire-Clay Brick

At 1300°C., the fire-clay brick show very little penetration. The slag has spread over the brick by wetting it, but some penetration, especially corrosion of the surface, occurred at 1400°C. This sharp decrease of resistance predicts that these brick would not be very effective for use at higher temperatures (Fig. 4).

The thin sections have shown that the majority of the iron oxide has been separated from the glassy matrix of the slag in the form of dendritic magnetite during cooling. A thin layer of reaction zone on the surface of the brick is observed by its dark color which separates it from the unattacked body.

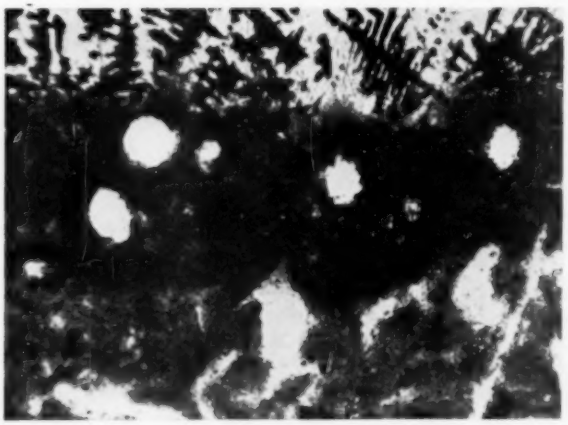

FIG. 7.—Photomicrograph of brick No. 3, showing slag, reaction zone, and unattacked body; at ordinary light.

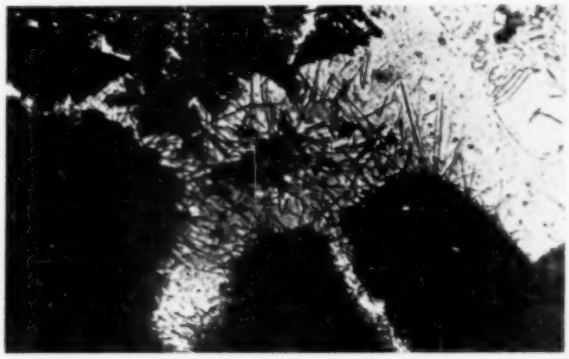

FIG. 8.—Brick No. 3, showing formation of large mullite crystals at brick-slag interface toward the slag; at ordinary light.

The surface irregularities or pores play an important role on thickness of the reaction zone. Although this zone generally constitutes an even layer, in some places where the brick surface provides weak points or holes the layer increases in depth.

The only definite crystal observed other than the brick grains previously mentioned is that of mullite, which forms a needle-like structure.

(*A*) *Mechanism of Mullite Formation:* There has been some discussion concerning the mechanism of mullite formation. Hugill and Green[8] show the mullite needles at the reaction face of the fire-clay brick exposed to the action of iron blast-furnace slag. Norton[15] gives a good picture of this problem in his study of porcelain bodies. He stresses the fact that the source of mullite crystals in a porcelain is undoubtedly the clay, since it is the only constituent which contains a sufficient amount of alumina to develop these crystals, and that all of the mullite crystals seem to have developed from inside the outline of the original feldspar grains. This formation could be explained by some sort of slow diffusion which makes the feldspar glass sufficiently rich in alumina that the mullite crystallizes out.

The present investigation affirms the explanation given by Norton.[15] The copper reverberatory slag plays the role of the feldspar glass already mentioned. The formation of the mullite crystals in the slag side of the slag-brick border implies the slow diffusion of alumina from the brick grains into the slag. This migration of alumina to neutralize the relative acidity of the slag is accelerated by the diffusion of iron oxide

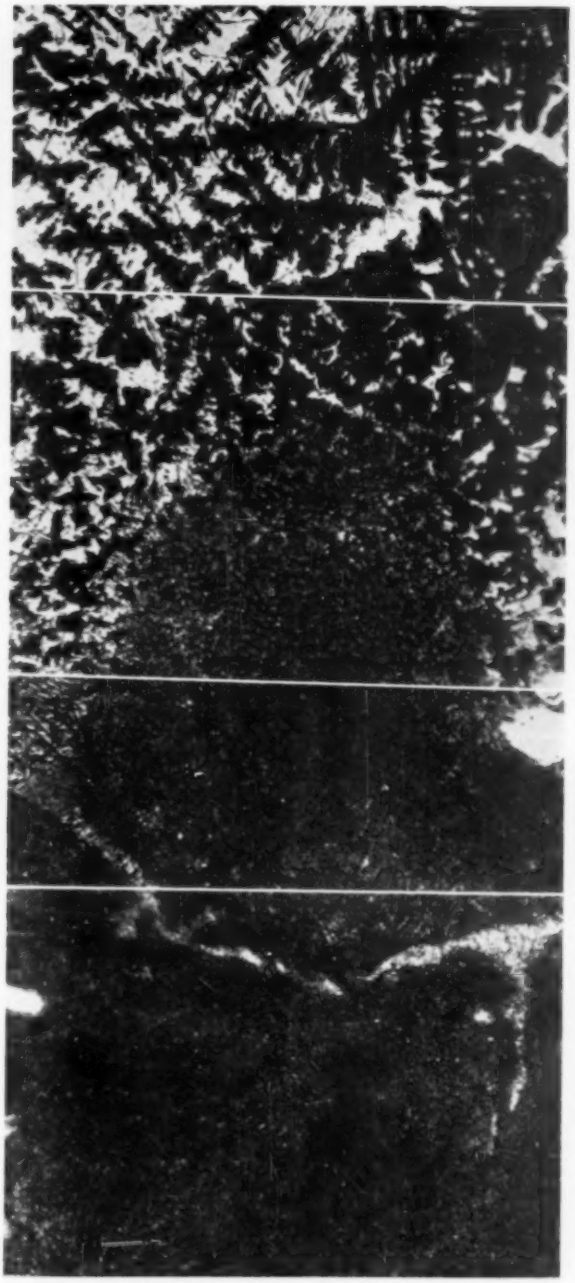

FIG. 9.—Brick No. 5, showing penetration of iron oxide inside brick grain; mullite crystals are formed outside of grain; at ordinary light.

[15] C. L. Norton, Jr., "Influence of Time on Maturing Temperature of Whiteware Bodies, II," *Jour. Amer. Ceram. Soc.*, **14** [2] 192–206 (1931).

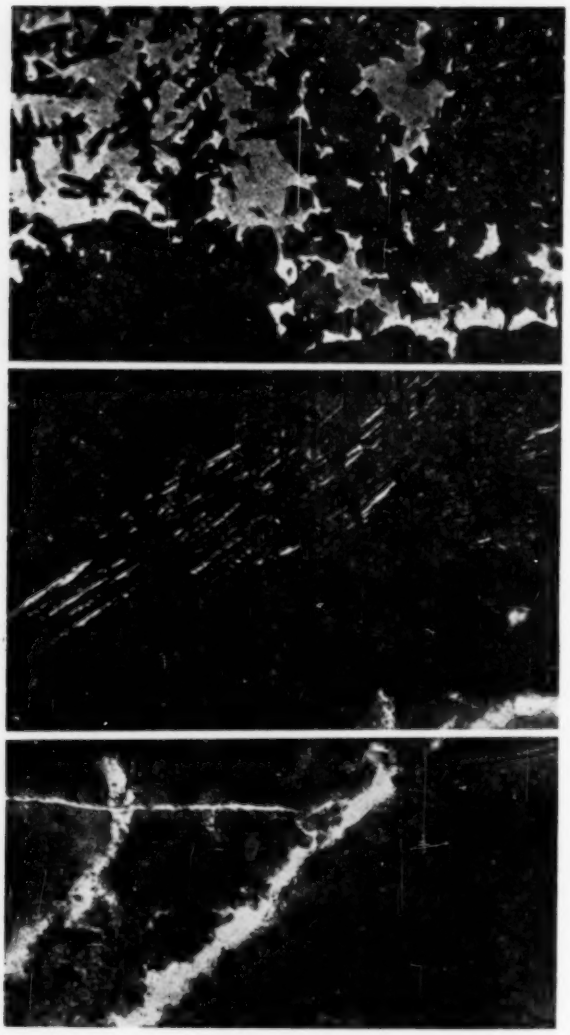

FIG. 10.—Brick No. 4, showing needle-like crystals and iron oxide dendrites in reaction zone; at ordinary light.

into the brick, in opposite direction, in order to decrease the difference of composition at both sides of the brick-slag border.

In two thin sections, those of brick Nos. 4 and 7, very characteristic crystals "of fibrous appearance, orienting themselves parallel to one another"[15] have been observed "inside the outline of the original clay grain."[15] Although this description coincides with that given by Peck[16] for the sillimanite crystals, Peck's photomicrographs seemed to show mullite crystals rather than sillimanite. Their separation inside the original boundary of the brick grains differentiate them from the other mullite crystals which are also at random orientation; but the parallel orientation in this case may well be due to twinning. These crystals, which are shown in brick No. 4 (Fig. 10), have a matrix formed by a complex iron, aluminum, and probably calcium

[16] A. B. Peck, "Effect of Time and Temperature on Microstructure of Porcelain," *Jour. Amer. Ceram. Soc.*, **2** [3] 175–94 (1919).

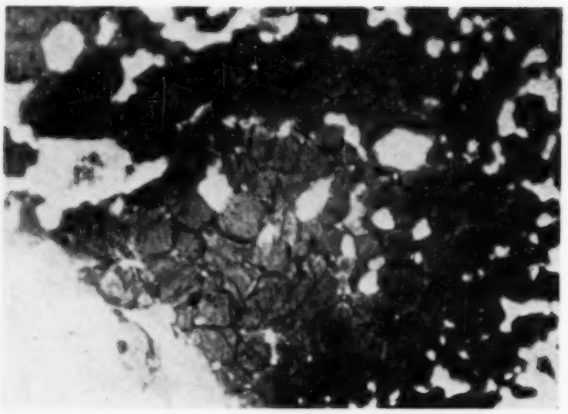

FIG. 11.—Brick No. 9, showing iron oxide penetration into a group of periclase crystals; at ordinary light.

silicate, containing also some magnetite dendrites. Although the author was unable to identify them definitely, it is plausible that they are still mullite crystals. By their formation, the remaining silica of the brick may have attracted the iron oxide and lime from the slag to form the dark-colored matrix.

(3) High-Alumina Brick

The general reaction scheme of high-alumina brick is similar to that of fire-clay brick. The set of the 1400°C. run shows that brick No. 7 is the most severely attacked of the fire-clay and alumina refractories. This is due to its definite basic behavior in the presence of the acid slag. The formation of mullite crystals is observed even between brick grains near, but outside of, the reaction zone.

(4) Magnesite Brick

Distinct zones of reaction and diffusion are observed in the magnesite brick. This, especially at the 1300°C. run, would give more credit to the fire-clay brick if the microstructures were not investigated. Study of the thin sections shows a dark slag matrix, contrasting with the fire-clay brick, followed by dark crystals in a highly birefringent matrix constituting the reaction zone. This zone contains the original groups of periclase crystals with their honeycomb structure. These groups are attacked by the penetrating slag, the iron oxide coloring them to a light reddish brown, which darkens toward the periphery where it becomes opaque. The individual crystals are larger than those in the unattacked zone. Two sets of distinct, perpendicular cleavages were observed in many cases. An extinction at 90-degree angles has been observed. But this possibility of orthorhombic pyroxene formation is very doubtful, since careful study shows that this double extinction is due to the very thin layer of a very birefringent matrix, probably olivine or forsterite, formed between individual crystals of periclase. To eliminate the doubts, an X-ray powder pattern of a sample from the reaction zone has been taken in a Debye-Scherrer camera. The X-ray studies prove that the majority of the crystals are still in the form of periclase, since all the major lines check the existence of

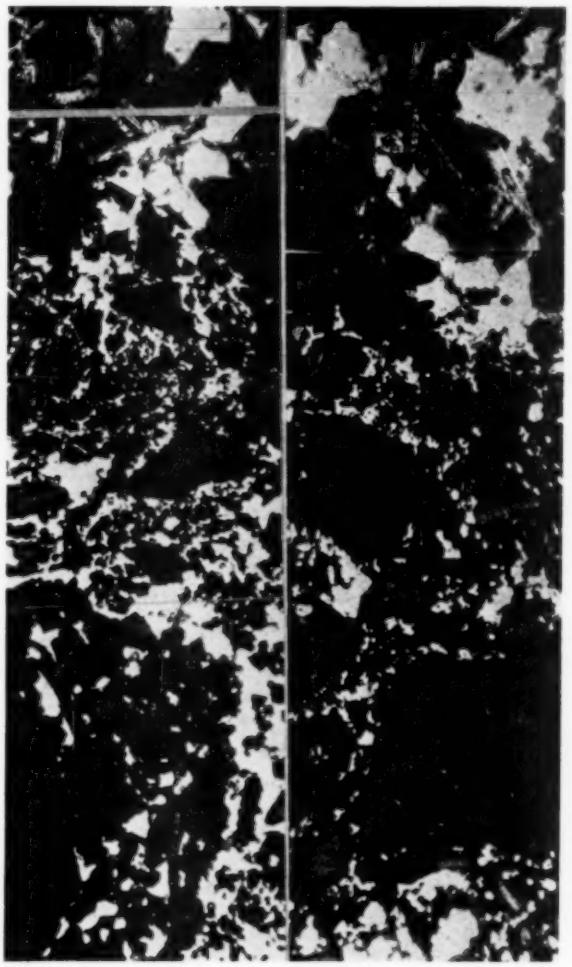

Fig. 12.—Joint of two chrome-magnesite brick taken from a blown-out copper reverberatory furnace; at ordinary light.

the latter. From these observations, the following mechanism of reaction may be concluded: As the slag penetrates through the pores, it forms olivine and forsterite crystals around the groups of periclase crystals. Since there is an excess of iron oxide in this zone, olivine may exceed the forsterite. The periclase crystals are probably in "solid solution with iron, together with some crystals of magnesioferrite," as in the case of magnesite brick in contact with iron or its oxides, explained by F. H. Norton.[17]

(5) Forsterite Brick

Next to the silica brick, the forsterite brick display the deepest diffusion zone. The contact surface between the slag and the brick is also appreciably corroded. The diffusion zone shows large and colorful olivine and forsterite crystals in the thin section. Although the forsterite has not been differentiated petrographically from the olivine, a good part of it is probably transformed gradually into olivine due to the reaction and absorption of iron.

When the magnesite brick is used, it will pass from the forsterite and olivine stage after a long period of use. The greater span of life of the magnesite brick constitutes a valuable advantage over the forsterite brick.

(6) Chrome Brick

The chrome brick shows a diffusion zone where the pores of the brick are filled by the slag. The study of the thin section reveals no corrosion of chromite crystals. In some sections, the magnetite from the penetrated slag shows a preferential orientation around the chromite crystals. The chrome brick seems to have little corrosion, but since it consists solely of a blend of ground chrome ores, molded under heavy pressure, the pores are subject to be filled with the slag.

(7) Chrome-Magnesite Brick

A thin section is made of the Ritex type chrome-magnesite brick, which is obtained from the smelting zone of a blown-out reverberatory furnace (Fig. 12). Large chrome crystals are still shown intact with some dark, iron-absorbed periclase crystals in a matrix of olivine and forsterite. The joint of the two brick was filled with large olivine crystals in a dark matrix of a complex silicate.

VI. Conclusions

(1) The porosity plays an important role in the behavior of the silica brick. Despite the acidic character of silica, the brick would not stand up very well in direct contact with the slag at higher temperatures.

(2) Although fire-clay brick behave satisfactorily at 1300°C., the increase of temperature has a marked effect on these brick; they are not to be suggested for high-temperature operations.

(3) The high-alumina brick are attacked more readily than the ordinary and superduty firebrick due to their porous and basic character.

(4) The forsterite brick is not to be suggested for this process due to its short life.

(5) The magnesite and chrome brick seem to be the most suitable. A close-packed mixture of coarse chrome grains and finely ground magnesite particles is also suggested; this brick would have a good slag resistance, low porosity, and low spalling tendency.

(6) Water-cooled jackets would increase the life of the furnace walls.

Acknowledgment

It is with great pleasure that the author takes this opportunity of acknowledging his indebtedness to C. R. Hayward for his invaluable guidance. The author also wishes to thank E. R. Marble, Jr., for supplying the slag and helpful data; and the Harbison-Walker Refractories Company for supplying the brick.

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[17] F. H. Norton, Refractories, p. 508, 2d ed. McGraw-Hill Book Co., Inc., New York, 1942. 798 pp.; *Ceram. Abs.*, **22** [6] 1032 (1943).

INFLUENCE OF VARIABLE AMOUNTS OF NEW YORK TALC, FLINT, AND CALCINED CLAY ON SERVICEABILITY OF GLAZED COOKING-WARE BODIES*

By Forrest Burnham and Milton A. Tuttle

Abstract

The effect of composition on the ability of glazed dishes to withstand thermal-shock treatments ordinarily received in cooking was studied. Bodies which gave best results contained approximately 10% of New York talc and also a small amount of calcined clay substituted for potters' flint. Bodies which had sufficiently high thermal expansion to throw the glaze into moderate or strong compression gave the best results. A terra sigillata finish applied to talc-free bodies was found to withstand autoclave treatment without crazing, and ware so made stood up very well in service tests.

I. Introduction

The purpose of this study was to determine by simulative service tests the suitability of a series of ceramic bodies for cooking-ware service, in which talc, flint, and calcined kaolin were variables. The services simulated were those encountered in baking, boiling, and deep frying.

II. Materials and Experimental Methods

(1) Body and Glaze Compositions

The series studied was developed from a talc-free body (body D1, Table I). Calcined kaolin was substituted for flint in increments of 12% from 0 to 36%. Talc was added to the various bodies in amounts of 10, 20, and 30%. The compositions of the various bodies are given in Table I.

Four glazes were tried on each of the sixteen bodies (once fired) to obtain one that would fit most of the bodies and pass an autoclave test of 150 lb. per sq. in. None of the glazes tried passed the test when applied to the talc-free bodies. The glaze that proved most satisfactory was one having the composition given in Table II.

A terra sigillata prepared from Alfred shale (red firing) was applied to the talc-free bodies and fired to cone 10. When subjected to the autoclave test, the finish did not craze as did the glazes. This finish was applied to ware made from bodies D1, D2, D3, and D4, and this ware was tested along with the regularly glazed ware.

(2) Preparation of Bodies and Specimens

The ball clays were blunged separately in excess water for 30 minutes and put through a 100-mesh sieve. The other ingredients were added, and the body was blunged for two hours. After putting through a 100-mesh sieve and filter pressing, the body was aged for two weeks.

Test dishes as illustrated in Fig. 1 were jiggered from the various bodies. These dishes were used for the service tests. Test pieces approximately 2 by 1 by $1\frac{1}{2}$ in. in size were used to study the firing behavior of the bodies and it was from these that tetrahedra for the expansion tests were made.

(3) Glazing and Firing

The firing behavior of the various bodies was determined by making a draw trial fire, and from these data it was decided to fire the glazed ware to cones 7, 8, and 9 and the terra sigillata ware to cone 10.

The glaze was sprayed on to a thickness of 0.032 ± 0.005 in. The terra sigillata was applied much thinner, approximately 0.015 in. All ware was once fired.

(4) Simulative Service Tests

After examining the glazed ware as it came from the kiln and eliminating all pieces that were crazed or otherwise defective, four service tests were run. In

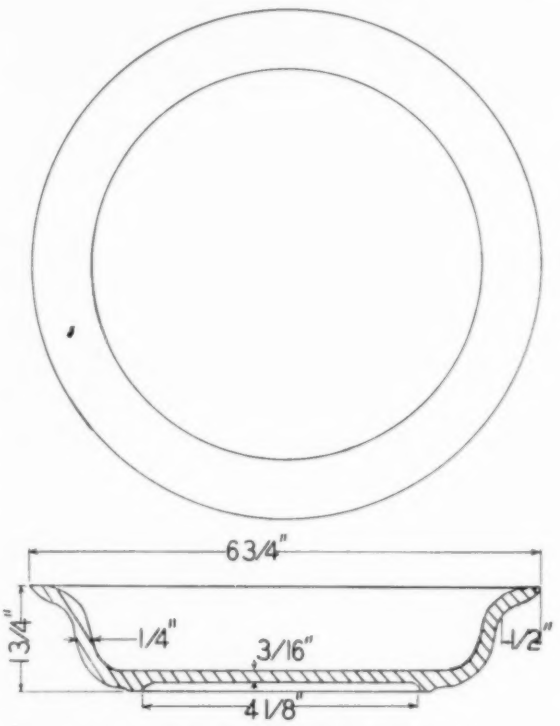

Fig. 1.—Test dish (jiggered dimensions).

* Presented at the Forty-Fifth Annual Meeting, The American Ceramic Society, Pittsburgh, Pa., April 21, 1943 (Design Division, formerly the Art Division). Received November 24, 1944.

TABLE I

BODY COMPOSITIONS (%)

Body No.	Ky. mixed ball clay	Ky. No. 5 ball clay	Ga. kaolin	N. C. kaolin (H S)	C & C ball clay	Buckingham feldspar	Flint	B & W 108 calcined Ga. kaolin	N. Y. talc
A1	6.30	4.90	7.97	7.00	10.50	8.13	25.20		30.00
A2	6.30	4.90	7.97	7.00	10.50	8.13	16.80	8.40	30.00
A3	6.30	4.90	7.97	7.00	10.50	8.13	8.40	16.80	30.00
A4	6.30	4.90	7.97	7.00	10.50	8.13		25.20	30.00
B1	7.20	5.60	9.11	8.00	12.00	9.29	28.80		20.00
B2	7.20	5.60	9.11	8.00	12.00	9.29	19.20	9.60	20.00
B3	7.20	5.60	9.11	8.00	12.00	9.29	9.60	19.60	20.00
B4	7.20	5.60	9.11	8.00	12.00	9.29		28.80	20.00
C1	8.10	6.30	10.25	9.00	13.50	10.45	32.40		10.00
C2	8.10	6.30	10.25	9.00	13.50	10.45	21.60	10.80	10.00
C3	8.10	6.30	10.25	9.00	13.50	10.45	10.80	21.60	10.00
C4	8.10	6.30	10.25	9.00	13.50	10.45		32.40	10.00
D1	9.00	7.00	11.40	10.00	15.00	11.60	36.00		
D2	9.00	7.00	11.40	10.00	15.00	11.60	24.00	12.00	
D3	9.00	7.00	11.40	10.00	15.00	11.60	12.00	24.00	
D4	9.00	7.00	11.40	10.00	15.00	11.60		36.00	

TABLE II

GLAZE COMPOSITION

	(%)		(%)
Talc (N. Y. State)	5.0	Whiting	5.0
Flint	20.6	Barium carbonate	12.6
Zinc oxide (calcined)	4.9	Ga. kaolin	7.1
Buckingham feldspar	40.0	Opax	4.8

TABLE III

FIRING AND FIRED PROPERTIES

Body No.	Absorption (%) at cone				Linear firing shrinkage (%) at cone			
	7	8	9	10	7	8	9	10
A1	2.3	0.8	0.5		7.7	7.6	7.4	
A2	2.2	<0.1	<0.1		9.2	9.0	9.1	
A3	0.8	0.7	0.7		10.8	10.8	10.2	
A4	2.5	<0.1	<0.1		10.8	10.8	10.2	
B1	2.2	<0.1	<0.1		9.0	8.9	8.4	
B2	4.7	3.1	2.0		8.9	8.9	9.5	
B3	4.0	1.6	1.2		9.5	9.8	9.5	
B4	1.8	<0.1	<0.1		12.6	12.6	11.8	
C1	1.1	<0.1	<0.1		9.4	9.5	9.5	
C2	3.5	2.4	1.3		11.4	11.4	10.7	
C3	2.0	<0.1	<0.1		11.6	11.6	12.6	
C4	1.9	0.8	0.8		12.1	13.2	13.7	
D1		7.3		2.8				9.2
D2		7.4		1.5				10.2
D3		7.7		3.2				10.8
D4		9.6						11.4

TABLE IV

THERMAL-EXPANSION CHARACTERISTICS OF BODIES

Fired to cone	Coefficient of expansion (× 10^{-6}) 40°–300°C.	300°–600°C.	40°–600°C.
	Body A1		
6	7.7	10.2	9.0
7	6.7	8.9	7.9
8	5.6	7.6	6.7
9	5.4	7.2	6.4
10	5.2	6.8	6.1
	Body A4		
6	6.4	6.5	6.5
7	5.5	5.9	5.7
8	4.6	5.2	4.9
9	3.7	4.5	4.1
10	2.7	3.8	3.3
	Body D1		
8	5.8	11.9	9.1
9*	6.1	11.0	8.7
10	6.3	10.1	8.3
	Body D4		
8	4.7	5.5	5.1
9*	5.1	5.6	5.3
10	5.4	5.7	5.5
	Body C2		
6	6.1	9.3	7.8
7	6.3	8.6	7.5
8	6.4	7.9	7.2
9	5.9	7.2	6.5
10	5.3	6.4	5.9
	Body C3		
6	5.8	6.6	6.2
7	5.9	6.6	6.3
8	5.9	6.6	6.3
9	5.3	6.3	5.8
10	4.7	5.9	5.3

* Interpolated; values for other cones in discussion were also interpolated.

all tests, any form of crazing, cracking, or chipping was considered as evidence of failure and the piece was eliminated.

Test No. 1: The empty dishes were placed in an oven operating at 260°C. (500°F.), held there for 30 minutes, drawn from the oven, placed on a cold iron plate, and allowed to cool to room temperature. This cycle was repeated 20 times or until failure.

Test No. 2: Those dishes passing test No. 1 were filled with water, placed on a gas plate, and allowed to remain until the water had boiled for 5 minutes. The dishes were then removed, placed on a cold iron plate, and allowed to cool to room temperature. This cycle was repeated 20 times or until failure.

Test No. 3: Those dishes passing tests Nos. 1 and 2 were filled with shortening and heated as in test No. 2 until the shortening had reached and maintained a temperature of 250°C. for 5 minutes. The dishes were then removed, placed on a cold iron plate, and allowed to cool to room temperature. This cycle was repeated 20 times or until failure.

Test No. 4: Those dishes passing tests Nos. 1, 2, and 3 were washed and again filled with water. They were

TABLE V

SUMMARY OF RESULTS OF SERVICE TESTS

	Body No.															
	A1	B1	C1	D1*	A2	B2	C2	D2*	A3	B3	C3	D3*	A4	B4	C4	D4*
Talc (%)	30	20	10		30	20	10		30	20	10		30	20	10	
Flint	25.2	28.8	32.4	36.0	16.8	19.2	21.6	24	8.4	8.6	10.8	12				
Kaolin, calcined (%)					8.4	9.6	10.8	12	16.8	19.2	21.6	24	25.2	28.8	32.4	36.0
Cone No.	Failure occurred in test No.															
7	3	3	3		3	3	4		1	3	3		2	3	0	
8	3	2	3		1	1	3		0	1	4		0	2	2	
9	2	1	3		0	0	4		0	0	3		0	0	0	
10				4				4				3				2
Avg.	2.7	2	3		1.3	1.3	3.7		0.3	1.3	3.3		0.7	0.2	0.7	

* Terra sigillata finish.

then heated as in the previous two tests until five minutes after the water had boiled away; the dishes were then removed, placed on a cold iron plate, and allowed to cool to room temperature. This cycle was repeated until failure.

(5) Thermal Expansion

Expansion characteristics of the more important bodies were determined by means of the interferometer.

III. Results

The firing shrinkages and absorptions of the bodies are given in Table III. The thermal-expansion characteristics of the more important bodies are given in Table IV. Table V shows a summary of the simulative service test data and gives the test number in which failure occurred for each body and temperature.

IV. Discussion of Results

(1) General Properties

All bodies jiggered well, dried safely, and showed about the same amount of linear drying shrinkage (3%). The talc bodies approached vitrification at (or about) cone 8, whereas the talc-free bodies showed an absorption of 1.5% or more at cone 12.

Adding talc in amounts of 10, 20, and 30% resulted in bodies with decreased firing shrinkage whereas substituting calcined kaolin for flint gave bodies with greater firing shrinkages. The firing shrinkages of the talc bodies at cone 8 varied from 7.6 to 13.2%, those of the most promising bodies (C 2 and C 3) approximating 11.5%. The difference in shrinkage between the cone 7 and cone 8 ware was negligible in practically all instances; when fired to cone 9, some bodies showed a decrease in shrinkage which is indicative of overfiring, though the ware in no other way appeared overfired.

(2) Thermal Expansion

The thermal-expansion data have been presented in Table IV in such manner as to show the characteristics over different temperature ranges. The expansions between 300° and 600°C. are considered to be particularly significant in light of the results of the service tests. The relation between the expansions in this range and serviceability is shown in Fig. 2. For

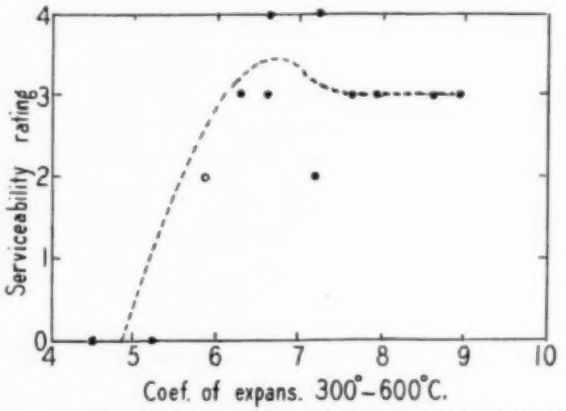

FIG. 2.—Relation between thermal expansion of bodies and serviceability of glazed cooking-ware bodies.

the types of ware under consideration, it is evidently desirable to have a coefficient of at least 6.3×10^{-6} over this range. Upon cooling, the glaze on such bodies was under such a high compression that expansion occurring during test heats did not overcome it readily. These results tie in well with the finding in the service test that flint is a very desirable ingredient in the bodies. The greater expansions of some bodies over this range are accounted for by the quartz inversion.

(3) Simulative Service Tests

These tests were carried out in such manner as to subject the dishes to increasingly severe conditions.

Test No. 1: In this test (empty in an oven at 250°C.), the dishes were heated inside and outside at the same time and cooled likewise. At no time during the test was opportunity given for any appreciable temperature gradient through the ware. All failures in this test were caused by crazing; the repeated heating and consequent expansions tended to release compression on the glaze and throw the glaze into tension. In general, the glazed bodies that failed in this test contained less than 20% of flint. The exceptions had an absorption of 1.8% or contained 10% of talc.

The four bodies coated with terra sigillata passed the test. Only one body with a coefficient of expansion as great as 6.3×10^{-6} over the range of 300° to 600°C. failed in this test.

Test No. 2: This test was more severe. The outside bottom of the dish was heated fast (practically in direct contact with a gas flame), while the inside surface (in contact with water) heated up much more slowly; an appreciable temperature gradient was thus set up through the piece. After the water began to boil, the gradient remained about the same and the dish did not become hotter. During cooling (on a cold iron plate), the outside was subjected to a greater temperature shock than the inside and again there was opportunity for appreciable temperature gradients. Though most of the failures in this test were due to crazing, a number of pieces cracked. As in the case of test No. 1, the repeated heatings tended to throw the glaze out of compression into tension, which resulted in crazing. Cracking was caused by the differential expansion between various portions of the piece.

The glazed bodies passing this test had an expansion coefficient (300° to 600°C.) greater than 6.3×10^{-6}. The test eliminated all flint-free bodies.

Test No. 3: The third test (heating shortening to 250°C.) caused the entire dish to reach a minimum temperature of 250°C., and the conditions of test No. 2 prevailed but at a higher temperature. To maintain the shortening at 250°C., a considerably higher temperature on the outside of the dish was required. Greater temperature gradients particularly on cooling down were possible. Most failures were due to cracking.

Only two glazed bodies (C2 and C3) passed this test. Both contained 10% of talc. One contained 21.6% of flint and 10.8% of calcined kaolin, whereas the other contained 10.8% of flint and 21.6% of calcined kaolin. The thermal expansion of each between 300° to 600°C. was greater than 6.6×10^{-6}.

Bodies D1 and D2 which were coated with terra sigillata passed this test. The expansion of both of these bodies was much greater than 6.6×10^{-6} over the range of 300° to 600°C.

Test No. 4: In this test, the dishes were allowed to remain dry over a gas burner for 5 minutes, which resulted in higher temperatures throughout the piece together with much greater temperature gradients. All failures were due to cracking. Both glazed bodies failed in the fifth cycle of this test, whereas the two bodies coated with terra sigillata failed in the first and second cycle.

(4) Body Composition

As expected, the glaze applied to the talc bodies did not craze in the autoclave test. On account of this result as well as those of the service tests, the use of talc in the glazed bodies under study is considered to be very important. The glazed ware that withstood the service tests best contained 10% of talc. Higher percentages were not advantageous. The thermal expansion of bodies containing 10% of talc did not vary with firing temperature as did those of bodies containing higher percentages of talc. Regarding the series studied, 10% of talc is the optimum percentage.

Flint was advantageous in the bodies because of the expansion characteristics it imparted to the ware (high expansion between 300° and 600°C.). In general, bodies containing less than 20% of flint showed up poorly in the service tests, the notable exception being body C3, which contained only 10.8% of flint but also 10% of talc.

There is no apparent outstanding advantage in using calcined clay in place of flint, although the best bodies, C2 and C3, contained 10.8% and 21.6% of clay, respectively. These bodies also contained talc and flint in important amounts.

(5) Terra Sigillata

The preliminary experiments showed that glazes applied to the talc-free bodies, D1, D2, D3, and D4, crazed when subjected to the autoclave test; however, terra sigillata applied to the same bodies did not craze in the autoclave test. These bodies expanded to such an extent as to cause the glazes to go into tension and craze but not sufficiently to cause the terra sigillata to craze. Inasmuch as the moisture expansion in both instances is the same, one of two things may occur: The terra sigillata is either under much greater compression or it is much stronger in tension than the glaze coat. The resistance of this type of coating to crazing is further shown by the manner in which coated bodies D1, D2, and D3 stood up in the service tests.

V. Summary

(1) A series of bodies, in which calcined kaolin was substituted for flint in various amounts and in which talc was added in amounts up to 30%, was studied with regard to the use of the bodies for glazed cooking ware.

(2) Table II gives the composition of the glaze used.

(3) The glazed ware that proved best in the series were bodies C2 and C3 given in Table III.

(4) Bodies having comparatively high thermal expansions in the range of 300° to 600°C. in general proved best in the series.

(5) A terra sigillata finish was found to resist autoclave treatment and service tests without crazing when applied to talc-free bodies whereas glazes on the same bodies crazed in the autoclave.

Acknowledgment

The authors wish to acknowledge the assistance of H. G. Schurecht and J. F. McMahon under whose direction the study was carried out.

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MOLYBDENUM IN ENAMELS: III, TYPICAL MOLYBDENUM ENAMELS*

By Karl Kautz

Abstract

Compositions and characteristics of various types of enamels using the most successful mill additions in Parts I and II are reported. The enamels used in this paper are (1) clear enamels (regular) for ground or colored coats, (2) clear enamels (acid resisting) for colored coats, (3) high lead clear enamels maturing below 1000°F., (4) raw or partially fritted enamels for ground or colored coats, and (5) white antimony enamels for direct application to the metal base. Reported for the first time are some white enamels containing molybdenum in the frit, which adhere to sheet steel without additions of molybdenum compounds to the mill.

I. Introduction

Since the publication of Parts I and II of this series of papers,[1] considerable work has been done in the development of enamels which might be used commercially. Some of these enamels have been plant-tested, and others are merely successful laboratory trials.

A series of clear enamels has been developed which mature at temperatures ranging from 1575° to 800°F. These enamels may be used as clear ground coats or as one-coat color bases. In some cases, principally at lower temperatures, one-coat white enamels may be made by milling in some opacifying material. Calcium molybdate has been found to produce good opacity and good adherence when milled into these low-temperature enamels.

A considerable amount of work has also been done on one-coat, acid-resistant enamels maturing at 1550° to 1600°F. Some of the most promising compositions in this field are given, although none has been completely successful owing to the highly viscous nature of this type of enamel.

Raw or partially fritted enamels are a definite possibility because the antimony oxide-molybdate mill additions can be used to promote adherence. Some enamels in this field are given.

White antimony enamels for direct application to steel are given at three maturing temperatures, 1525°F., 1475°F., and 1400°F.

One of the most recent developments has been white molybdenum enamel maturing in the range of 1500° to 1300°F. Molybdenum trioxide smelted into these enamels produced excellent opacity and adherence in single coats applied directly on sheet steel or cast iron.

II. Clear Enamels

1575°F.: A clear ground coat or color base at this temperature is as follows:

Empirical formula

$$\left.\begin{matrix}0.20\ K_2O\\0.45\ Na_2O\\0.25\ CaF_2\\0.10\ BaO\end{matrix}\right\}0.20\ Al_2O_3\left\{\begin{matrix}2.40\ SiO_2\\0.60\ B_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax	32.4	Soda ash	4.5
Feldspar	31.6	Fluorite	5.5
Quartz	20.4	Barium carbonate	5.6
			100.0

1525°F.: A clear ground coat or color base at this temperature is as follows:

Empirical formula

$$\left.\begin{matrix}0.15\ K_2O\\0.50\ Na_2O\\0.25\ CaF_2\\0.10\ BaO\end{matrix}\right\}0.15\ Al_2O_3\left\{\begin{matrix}1.50\ SiO_2\\0.50\ B_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax	34.0	Soda ash	9.5
Feldspar	29.8	Fluorite	6.9
Quartz	12.8	Barium carbonate	7.0
			100.0

1475°F.: A clear ground coat or color base at this temperature is as follows:

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.55\ Na_2O\\0.25\ CaF_2\\0.10\ BaO\end{matrix}\right\}0.10\ Al_2O_3\left\{\begin{matrix}1.20\ SiO_2\\0.40\ B_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax	31.2	Soda ash	15.2
Feldspar	22.8	Fluorite	8.0
Quartz	14.7	Barium carbonate	8.1
			100.0

Mill batches for the foregoing clear enamels maturing at 1575°F., 1525°F., and 1475°F. are quite similar. A typical batch is as follows: Frit 100, clay 6 to 7, electrolyte 0.25, barium molybdate* 1.50, calcined antimony trioxide 1.50, and water 45 parts.

* Lead molybdate (2 parts), calcium molybdate (1 part), or sodium molybdate (1 part) may be substituted for barium molybdate in this batch.

Note: Antimony trioxide calcined at 1100°F. behaves better as a mill addition than the raw oxide.

* Preprinted for the Forty-Seventh Annual Meeting, The American Ceramic Society, 1945 (Enamel Division). Received January 4, 1945.

[1] (*a*) Karl Kautz, "Molybdenum in Enamels: I, Adherence Produced with Molybdenum Compounds," *Jour. Amer. Ceram. Soc.*, **23** [10] 283–87 (1940).

(*b*) Karl Kautz, "Molybdenum in Enamels: II, Adherence Produced with Soluble and Insoluble Molybdates," *ibid.*, **25** [6] 160–63 (March 15, 1942).

1400°F.: Opaline enamels at this temperature are given, which may be used for ground coats, color bases, or white coats; these enamels adhere equally well to sheet steel or cast iron.

(A) CRYOLITE TYPE

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.25\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.20\ BaO\\0.15\ ZnO\end{matrix}\right\}\ \left.\begin{matrix}0.10\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\right\}\ \left.\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\end{matrix}\right\}$$

Smelter batch (%)

Borax	24.4	Cryolite	8.9
Feldspar	23.7	Fluorite	5.0
Quartz	11.5	Barium carbonate	16.8
Soda ash	4.5	Zinc oxide	5.2
			100.0

(B) FLUORITE TYPE

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.35\ Na_2O\\0.35\ CaF_2\\0.20\ BaO\end{matrix}\right\}\ 0.10\ Al_2O_3\ \left\{\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax	24.5	Soda niter	7.3
Feldspar	23.7	Fluorite	11.6
Quartz	11.5	Barium carbonate	16.8
Soda ash	4.6		
			100.0

The mill batch for the ground coat is frit A (or B) 100, clay 4, sodium nitrite 0.25, lead molybdate 2, calcined antimony oxide 1.50, and water 45 parts. For colors, add 2 to 4% of ceramic pigments to this batch.

The mill batch for white enamel is frit A (or B) 100, clay 4, calcium molybdate 6 to 10, and water 45 parts. This batch may be used as a cover coat or as a white coat applied directly to the steel or cast-iron base.

1300°F.: An opaline enamel, similar to the foregoing enamels but maturing at 1300°F., is as follows:

Empirical formula

$$\left.\begin{matrix}0.075\ K_2O\\0.200\ Na_2O\\0.075\ Na_2F_2\\0.150\ CaF_2\\0.200\ BaO\\0.200\ ZnO\\0.100\ CaO\end{matrix}\right\}\ \left.\begin{matrix}0.075\ Al_2O_3\\0.025\ Al_2F_6\end{matrix}\right\}\ \left.\begin{matrix}0.75\ SiO_2\\0.25\ B_2O_3\end{matrix}\right\}$$

Smelter batch (%)

Borax	23.5	Fluorite	5.7
Feldspar	20.5	Barium carbonate	19.4
Quartz	8.9	Zinc oxide	8.0
Soda ash	3.9	Calcium carbonate	4.9
Cryolite	5.2		
			100.0

The mill batch is frit 100, clay 4, lead molybdate 2.0, calcined antimony oxide 1.50, and water 45 parts.

Like the enamels maturing at 1400°F., this enamel may be used as a ground coat, color base, or white coat for direct application to sheet steel or cast iron. Calcium molybdate may be used as a mill addition for opacity and adherence, but, owing to its refractory nature, it usually raises the maturing temperature.

800°–1000°F.: Clear enamels high in lead oxide may be used on sheet steel, cast iron, or copper at temperatures ranging from 800° to 1000°F. "Antimonyl molybdate," as a mill addition, produced excellent adherence in these enamels as low as 800°F. Lead molybdate and antimony oxide likewise produced excellent adherence but raised the maturing temperature to 870°F. Large amounts of lead molybdate produced a cream-white opaque enamel with good adherence at about 920°F. Technical molybdenum trioxide smelted in these enamels produced excellent adherence to sheet steel when applied by conventional methods and also by molten-spray and molten-dip methods. These enamels, owing to their high lead content, should not be used on surfaces which come in contact with food or drinking water, but they might find application as weather-resistant coatings for many products. The clear enamel given next has good acid-resisting properties and should be weather resistant; it was applied with a paint brush to black structural steel shapes (free from loose rust) and gave excellent adherence when fused with a gas-air torch. Because the enamels have a light yellow-brown color, brown and tan ceramic pigments were used in some trials to produce thin protective coatings on both sheet steel and cast iron.

This clear enamel has the following composition:

Empirical formula

$$\left.\begin{matrix}0.85\ PbO\\0.05\ ZnO\\0.05\ CaF_2\\0.05\ Li_2O\end{matrix}\right\}\ \cdots\cdots\ \left\{\begin{matrix}0.30\ SiO_2\\0.25\ B_2O_3\end{matrix}\right.$$

Smelter batch (%)

Litharge	75.80	Lithium carbonate	1.46
Zinc oxide	1.60	Quartz	7.20
Fluorite	1.54	Boric acid	12.40
			100.00

The addition of 4 to 8% of technical molybdenum trioxide to this smelter batch is optional.

The mill batch is composed of frit 100, clay 3, antimonyl molybdate 2.6, and water 40 parts (fire 10 minutes at 800°F.). (Lead molybdate (2 parts) and antimony trioxide (1½ parts) may be substituted for antimonyl molybdate in this batch.)

For a light-colored opaque coating, 8 parts of lead molybdate may be substituted for antimonyl molybdate. When the frit contains MoO_3, additions of molybdenum compounds or antimony oxide to the mill are unnecessary for good adherence.

III. Acid-Resisting Clear Enamels

Considerable work with acid-resisting enamels showed that good adherence can be obtained in these enamels with a mill addition of antimony trioxide and one of the molybdates, such as barium. Characteristic of these enamels are the blisters and copperheads produced during the "primary boiling" stage. These enamels must necessarily contain high silica and this in turn produces a highly viscous melt at the firing

temperature. The escape of gases from the steel base during the firing operation produces large blisters which either refuse to flow together or do so, after some delay, so that copperheads are formed. Attempts to lower the viscosity usually resulted in a decrease of acid resistance. A method for reducing the evolution of gases from the steel base would undoubtedly be beneficial, not only in these acid-resistant enamels but in any enamel coating applied directly to steel. An etched steel surface, however, is desirable for the best adherence. Some attempts to free the sheet steel of gases by scaling in air followed by etching in oxidizing acids showed encouraging results.

An accepted acid-resistant enamel of the following composition was used:

Empirical formula

$$\left.\begin{matrix}0.2\ K_2O\\0.3\ Na_2O\\0.5\ CaF_2\end{matrix}\right\} \cdots\cdots \left\{\begin{matrix}2.50\ SiO_2\\0.20\ B_2O_3\end{matrix}\right.$$

Calculated percentage composition, melted

SiO_2	62.40	Na_2O	7.74
B_2O_3	5.82	CaF_2	16.22
K_2O	7.82		

Smelter batch (%)

Borax	13.2	Fluorite	13.5
Soda ash	7.3	Quartz	52.0
Potash niter	14.0		
			100.0

This enamel was stainless with citric acid, but was very viscous and refractory. The SiO_2, B_2O_3, and CaF_2 contents were then changed to make an enamel of lower viscosity but still with good acid resistance; this composition was as follows:

Empirical formula

$$\left.\begin{matrix}0.2\ K_2O\\0.3\ Na_2O\\0.2\ CaO\\0.3\ CaF_2\end{matrix}\right\} \cdots\cdots \left\{\begin{matrix}2.40\ SiO_2\\0.30\ B_2O_3\end{matrix}\right.$$

Calculated percentage composition, melted

SiO_2	60.80	CaO	4.72
B_2O_3	8.85	Na_2O	7.85
CaF_2	9.85	K_2O	7.93
			100.00

Smelter batch (%)

Borax	19.0	Calcium carbonate	6.7
Soda ash	5.3	Fluorite	7.8
Potash niter	13.4	Quartz	47.8
			100.0

This enamel had good acid-resistant properties and good adherence, but it had a tendency to blister when used as a single coat directly on steel. A further alteration in the SiO_2, B_2O_3, Na_2O, and CaF_2 contents produced an enamel of acceptable viscosity or fluidity but with decreased acid-resistant properties. This enamel was as follows:

Empirical formula

$$\left.\begin{matrix}0.2\ K_2O\\0.2\ Na_2O\\0.1\ ZnO\\0.5\ CaF_2\end{matrix}\right\} \cdots\cdots \left\{\begin{matrix}2.00\ SiO_2\\0.40\ B_2O_3\end{matrix}\right.$$

Calculated percentage composition, melted

SiO_2	53.0	ZnO	3.6
B_2O_3	12.3	Na_2O	5.5
CaF_2	17.3	K_2O	8.3
			100.0

Smelter batch (%)

Borax	26.9	Fluorite	13.7
Potash niter	14.2	Quartz	42.3
Zinc oxide	2.9		
			100.0

The B_2O_3:SiO_2 ratio seems to be very important in determining the fluidity and acid resistance in this type of enamel. The first enamel had a B_2O_3:SiO_2 molecular ratio of 1:12½ and was very viscous but quite acid resisting. In the second enamel, the B_2O_3:SiO_2 ratio was 1:8; this enamel had greater fluidity than the first while still maintaining good acid-resisting properties. The B_2O_3:SiO_2 ratio of the third enamel was 1:5, which reduced the viscosity to the point where smooth coatings, free from blisters and large copperheads were obtained but at the expense of acid resistance. From these, and other tests, it is concluded that the molecular ratio, B_2O_3:SiO_2, should not be lower than 1:7 if good acid-resisting properties are to be expected in this type of enamel.

The mill batch used in these trials was frit 100, clay 1.5, bentonite 0.3, ammonium carbonate 0.25, barium molybdate 1.5 (or $PbMoO_4$ = 2.0), calcined antimony trioxide 1.5, and water 45 parts.

IV. Raw Enamels

Because mill additions of antimony oxide and a molybdate (such as lead, barium, calcium, or sodium) produce adherence in clear and white enamels, it was believed that satisfactory ground coats, color coats, or white coats could be produced by milling the raw (unsmelted) ingredients together. Of course, soluble ingredients and other ingredients which give off gases or water vapor when heated cannot be used. This, then, eliminates all soluble compounds, all carbonates, and most compounds (clay excepted) containing water of crystallization and allows only a limited number of compounds to be used in compounding these enamels. Minerals, or compounds, such as feldspar, nepheline syenite, quartz, clay, cryolite, fluorite, zinc oxide, and lead oxide naturally can be used, but none of these compounds contains B_2O_3, so necessary for successful enamels.

Compounds containing B_2O_3, which are commercially available, are borax ($Na_2O \cdot 2B_2O_3 \cdot 10H_2O$) and boric acid ($B_2O_3 \cdot 3H_2O$), but both of these compounds are soluble and contain water of crystallization and therefore cannot be used. The borates of the alkaline earths (barium, calcium, and magnesium) are insoluble, but they contain large amounts of water of crystallization. Lead, lithium, and zinc metaborates contain no water of crystallization, and are insoluble, sparingly soluble, and soluble, respectively.

Colemanite, a mineral having the formula $2CaO \cdot 3B_2O_3 \cdot 5H_2O$, was tried in these raw enamels but produced tearing and blistering owing to the escape

TABLE I

PARTIALLY FRITTED ENAMELS

Enamel No.	(3)	(4)	(5)	(6)	(7)	(8)
	Empirical formulas (%)					
K_2O	0.10	0.10	0.10	0.10	0.10	0.05
Na_2O	0.15	0.20	0.25	0.30	0.35	0.40
CaO	0.15	0.20	0.25	0.30	0.35	0.40
Na_2F_2	0.30	0.30	0.30	0.20	0.20	
CaF_2	0.15	0.10				0.05
ZnO	0.15	0.10	0.10	0.10		0.10
Al_2O_3	0.15	0.15	0.15	0.15	0.15	0.10
AlF_3	0.10	0.10	0.10	0.066	0.066	
B_2O_3	0.30	0.40	0.50	0.60	0.70	0.80
SiO_2	1.30	1.50	1.70	1.90	2.10	2.00
	Mill batches					
Soda-lime borosilicate	35.8	44.0	51.2	58.8	64.4	79.2
Feldspar	26.6	24.6	23.0	21.9	20.6	11.0
Clay	6.2	5.7	5.3	5.1	4.7	5.1
Cryolite	20.0	18.6	17.2	11.0	10.3	
Calcined fluorite	5.6	3.5				1.5
Calcined zinc oxide	5.8	3.6	3.3	3.2		3.2
Total	100.0	100.0	100.0	100.0	100.0	100.0
Sodium pyrophosphate	0.25	0.25	0.25	0.25	0.25	0.25
Barium molybdate	1.5	1.5	1.5	1.5	1.5	1.5
Calcined antimony oxide	1.5	1.5	1.5	1.5	1.5	1.5
Water	50.0	50.0	50.0	50.0	50.0	50.0

NOTE: Sodium pyrophosphate and barium molybdate used in these batches may be replaced by one part of sodium molybdate.

of water vapor when heated. A synthetic colemanite, $2CaO \cdot 3B_2O_3$, was smelted and tried experimentally in a raw enamel. This fritted compound apparently became hydrated upon milling or it decomposed into boric acid and calcium metaborate and produced tearing and blisters similar to colemanite. Boric acid and the stoichiometrical amount of CaO, or BaO, to form insoluble compounds were added to the mill without success. Barium borate, $3BaO \cdot 5B_2O_3 \cdot 6H_2O$, was made by precipitating a hot solution of borax with barium chloride, but this failed to give an enamel free from blistering and tearing.

Because the natural and precipitated insoluble borates of the alkaline earths failed to function and also because lead borate, or lithium borate, would be expensive, it was decided to make a frit containing the necessary amount of B_2O_3. An inexpensive frit for incorporating B_2O_3 into these raw, or (now) partially fritted enamels, is soda-lime borosilicate having the empirical formula of $Na_2O \cdot CaO \cdot 2B_2O_3 \cdot 4SiO_2$.

Smelter batch (%)	
Borax	53
Calcium carbonate	14
Quartz	33
	100

This frit is easily handled as a source of B_2O_3 and can be incorporated into most enamel compositions. Its major drawback is that it is not completely insoluble when milled. Some promising ground and color coats, however, were made using this glass. The empirical formulas and mill batches for these enamels are given in Table I.

The firing temperatures of these enamels ranged between 1500°F. and 1600°F. The grinding time depends on the amount of soda-lime borosilicate used. Generally, they can be ground in one sixth to one half the time necessary for 100% fritted enamels. In fact, overgrinding is difficult to prevent, especially for draining ground coats, because most materials added are minus 200-mesh. The draining properties of these enamels undoubtedly could be improved if coarser (about 140-mesh) feldspar and quartz were used in the mill batch.

Some promising one-coat colored enamels were made by milling 2 to 4% of ceramic pigments into these batches. One-coat white enamels were not entirely successful because of black specking. Good adherence, however, was obtained in most of the white enamels attempted. A semibright, white cover coat was compounded, having the following empirical and batch formulas:

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.30\ Na_2O\\0.25\ CaO\\0.25\ Na_2F_2\\0.10\ ZnO\end{matrix}\right\}\ 0.15\ Al_2O_3\ \left\{\begin{matrix}1.70\ SiO_2\\0.50\ B_2O_3\\0.05\ Sb_2O_5\end{matrix}\right.$$
$$0.083\ AlF_3$$

Mill batch (parts)			
Soda-lime borosilicate	48.8	Sodium nitrite	0.5
Feldspar	21.8	Zirconium opacifier	6.0
Clay	5.0	Water	50.0
Sodium meta-antimonate	7.5		
Cryolite	13.7		
Calcined zinc oxide	3.2		
	100.0		

This enamel fired to a good white with a semibright finish when applied over enamel No. 5 of Table I.

Other borosilicate glasses, less soluble than the foregoing, were tried experimentally. Some of these gave promising results when incorporated into various raw

batches. Because space does not permit the complete listing of these frits and raw batches, only the empirical formulas are given.

(1) $Na_2O \cdot CaO \cdot {}^1/_2Al_2O_3 \cdot 2B_2O_3 \cdot 5SiO_2$
(2) $Na_2O \cdot CaF_2 \cdot 2B_2O_3 \cdot 5SiO_2$
(3) $Na_2O \cdot CaF_2 \cdot BaO \cdot 2B_2O_3 \cdot 5SiO_2$
(4) $Na_2O \cdot {}^1/_2CaF_2 \cdot {}^1/_2BaO \cdot {}^1/_2Al_2O_3 \cdot 2B_2O_3 \cdot 5SiO_2$
(5) $Na_2O \cdot CaF_2 \cdot {}^4/_{10}Al_2O_3 \cdot 2B_2O_3 \cdot 4SiO_2$

The metaborates of the alkaline earths are insoluble, and it has been found that they hydrate slowly during milling and aging. A very fluid, low-temperature, insoluble borate glass is calcium barium metafluoborate having the empirical formula of $CaF_2 \cdot BaO \cdot 2B_2O_3$. Raw ground-coat enamels made with this glass incorporated in the batch had excellent adherence, wide firing range, and a tendency to tear.

V. White Antimony Enamels

White antimony enamels for direct application to steel were reported in Part II of this series of papers.[1(b)] Additional work in this field has been done, and below are reported several compositions at 1525°F. and one each at 1475°F. and 1400°F. Applied on deeply etched sheet steel, these enamels give excellent adherence in the laboratory trials; in heavy applications, they are free from black specks. They are characterized by a high content of sodium meta-antimonate, which generally causes decreased fluidity, or mobility, at firing temperatures. Much is still to be desired in increased mobility in this type of enamel. At lower temperatures, less sodium meta-antimonate is required to produce equivalent opacity and thus increased fluidity is obtained. At lower temperatures, moreover, black specking due to the escape of gases from the steel base is greatly reduced.

1525°F.: A white antimony enamel for direct application to the steel base at this temperature is as follows:

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.50\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.10\ BaO\end{matrix}\right\}\ \begin{matrix}0.10\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\ \left\{\begin{matrix}2.10\ SiO_2\\0.60\ B_2O_3\\0.15\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax	30.2	Sodium nitrate	2.3
Feldspar	14.7	Cryolite	5.5
Quartz	23.7	Fluorite	3.1
Sodium meta-antimonate	15.3	Barium carbonate	5.2
			100.0

Another enamel fired at 1525°F. but with higher Sb_2O_5 content is as follows:

Empirical formula

$$\left.\begin{matrix}0.05\ K_2O\\0.55\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.10\ BaO\end{matrix}\right\}\ \begin{matrix}0.05\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\ \left\{\begin{matrix}2.10\ SiO_2\\0.60\ B_2O_3\\0.20\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax	29.5	Sodium nitrate	2.2
Feldspar	7.2	Cryolite	5.4
Quartz	27.8	Fluorite	3.0
Sodium meta-antimonate	19.8	Barium carbonate	5.1
			100.0

1475°F.: An enamel at this temperature similar to that preceding but containing less SiO_2, B_2O_3, and Sb_2O_5 is as follows:

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.30\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.20\ BaO\\0.10\ ZnO\end{matrix}\right\}\ \begin{matrix}0.10\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\ \left\{\begin{matrix}1.40\ SiO_2\\0.40\ B_2O_3\\0.10\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax	25.6	Cryolite	7.0
Feldspar	18.7	Fluorite	3.9
Quartz	16.0	Barium carbonate	13.2
Sodium meta-antimonate	12.9	Zinc oxide	2.7
			100.0

1400°F.: At this temperature, a white antimony enamel for direct application to the steel base is as follows:

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.25\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.20\ BaO\\0.15\ ZnO\end{matrix}\right\}\ \begin{matrix}0.10\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\ \left\{\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\\0.10\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax	21.8	Cryolite	8.0
Feldspar	21.2	Fluorite	4.4
Quartz	10.3	Barium carbonate	15.0
Sodium meta-antimonate	14.7	Zinc oxide	4.6
			100.0

A typical mill batch for these white antimony enamels is frit 100, clay 5, sodium nitrite 0.25, lead molybdate 2.5, and water 50 parts.

Substitutes for lead molybdate are 2 parts barium molybdate or 1.4 parts sodium molybdate. At 1400°F. and 1475°F., 6 parts of calcium molybdate were substituted for lead molybdate giving excellent adherence and increased opacity.

VI. White Molybdenum Enamels

At temperatures ranging from 1300° to 1500°F., white enamels, having excellent opacity and adherence to both sheet steel and cast iron and high fluidity, can be made by smelting molybdenum trioxide into a typical fluoric-opaline enamel. Molybdenum trioxide dissolves in these low-temperature enamels during smelting much as zircon does in certain types of enamels. The melt comes from the smelter, or crucible, as a transparent glass which turns white on cooling or quenching. In some compositions, the MoO_3 remains in solution in the quenched glass; in others, it partially separates as a white compound, possibly as a molybdate of calcium, barium, or zinc. Good adherence is obtained with as little as 1% of MoO_3 (0.02 equivalent MoO_3) smelted into the batch but its opacity is low. Good adherence and good opacity are obtained with $3^1/_2$% of MoO_3 (0.06 equivalent of MoO_3) smelted into some enamel compositions. The highest amount of molybdenum trioxide used in any

of these trials was 6.4% (0.10 equivalent of MoO_3). This amount gave excellent opacity and adherence but increased the maturing temperature and decreased the mobility to the point where black specks occasionally were encountered.

It has been found that the lower-cost technical molybdenum trioxide (chemical grade) can be used successfully when smelted into these enamels. The extremely small amount of Fe_2O_3 and other metal oxides contained in this grade apparently has little effect on the color of the enamel. The composition of the enamel had a decided effect on the quality of whiteness produced; some enamels were blue-white, others were pink-white, and some were cream-white. These enamels are very sensitive to firing conditions and should be fired in a strongly oxidizing furnace atmosphere. Reducing atmospheres produce a blue coloration due to the reduction of MoO_3 to a lower oxide, and sulfur gases cause pitting and blistering.

The most successful compositions in this field are characterized by low alumina and high fluorine. The fluorine may be incorporated as cryolite, fluorite, or sodium fluosilicate, or a combination of these. High fluorine means careful, low-temperature smelting to retain as much fluorine as possible in the frit. The enamels should also be as low in alkalis as practical to decrease water solubility of the frit. It has been found that P_2O_5 causes a serious reduction of adherence.

Because molybdenum trioxide dissolves in enamels like zircon, enamels containing both of these compounds are practical. Sodium meta-antimonate may also be used in combination with MoO_3 to increase opacity in these enamels. Enamels in this field thus may contain molybdenum trioxide only, molybdenum trioxide and zircon, molybdenum trioxide and sodium antimonate, or possibly all three.

These enamels are usually milled with water and clay (4 to 5 parts) to which an electrolyte is sometimes added. Sodium nitrite, sodium pyrophosphate, and lime have been used successfully.

At the low temperatures used, acid-resistant enamels are out of the question, because enough SiO_2 to produce good acid-resisting properties cannot be incorporated. Weather-resistant enamels, however, which could be applied commercially to a large number of products, can be made in this firing range.

The compositions of five types of white molybdenum enamels are given; these are (1) cryolite, (2) fluorite, (3) sodium fluosilicate, (4) zircon, and (5) sodium meta-antimonate. These compositions may be altered within wide ranges if necessary.

(1) Cryolite Type at 1400°–1450°F.

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.25\ Na_2O\\0.15\ Na_2F_2\\0.20\ BaO\\0.15\ ZnO\\0.15\ CaF_2\end{matrix}\right\}\ 0.10\ Al_2O_3\ \left\{\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\\0.06\ MoO_3{}^*\end{matrix}\right.\quad \left\{\begin{matrix}0.05\ Al_2F_6\end{matrix}\right.$$

	Smelter batches (%) 0.06 MoO_3	0.02 MoO_3	0.10 MoO_3
Borax	23.6	24.1	23.0
Feldspar	22.9	23.4	22.4
Quartz	11.1	11.4	10.8
Soda ash	4.3	4.5	4.2
Cryolite	8.6	8.8	8.4
Fluorite	4.8	4.9	4.7
Barium carbonate	16.2	16.6	15.8
Zinc oxide	5.0	5.1	4.9
Molybdenum trioxide*	3.5	1.2	5.8
	100.0	100.0	100.0

* Molybdenum trioxide is given as the sublimed grade. If technical grade is used, a greater amount is needed because this grade contains approximately 90% MoO_3. Because the technical grade often contains molybdenum dioxide (MoO_2), it is better, when using this grade, to replace part of the soda ash with the equivalent amount of sodium nitrate.

(2) Fluorite Type at 1400°–1450°F.

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.35\ Na_2O\\0.35\ CaF_2\\0.20\ BaO\end{matrix}\right\}\ 0.10\ Al_2O_3\ \left\{\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\\0.10\ MoO_3\end{matrix}\right.$$

Smelter batch (%)

Borax	22.9	Soda niter	6.8
Feldspar	22.2	Fluorite	10.9
Quartz	10.8	Barium carbonate	15.7
Soda ash	4.3	Molybdenum trioxide (technical)	6.4
			100.0

(3) Sodium Fluosilicate Type at 1400°–1450°F.

Empirical formula

$$\left.\begin{matrix}0.05\ K_2O\\0.30\ Na_2O\\0.20\ Na_2F_2\\0.20\ CaF_2\\0.20\ BaO\\0.05\ M_gO\end{matrix}\right\}\ 0.05\ Al_2O_3\ \left\{\begin{matrix}0.90\ SiO_2\\0.20\ SiF_4\\0.30\ B_2O_3\\0.10\ MoO_3\end{matrix}\right.$$

Smelter batch (%)

Borax	22.7	Sodium fluosilicate	14.9
Feldspar	11.0	Fluorite	6.2
Quartz	14.2	Barium carbonate	15.6
Soda ash	4.2	Magnesium carbonate	1.6
Soda niter	3.3	Molybdenum trioxide (technical)	6.3
			100.0

(4) Zircon Type at 1400°–1450°F.

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.25\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.20\ BaO\\0.15\ ZnO\end{matrix}\right\}\ \left\{\begin{matrix}0.10\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\right.\quad \left\{\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\\0.10\ ZrO_2\\0.05\ MoO_3\end{matrix}\right.$$

Smelter batch (%)

Borax	22.0	Cryolite	8.0
Feldspar	21.3	Fluorite	4.5
Quartz	8.0	Barium carbonate	15.1
Zircon	7.0	Zinc oxide	4.6
Soda niter	6.5	Molybdenum trioxide (technical)	3.0
			100.0

* Batches for 0.02 MoO_3 and 0.10 MoO_3 are also given.

(5) SODIUM META-ANTIMONATE TYPE AT 1400°–1450°F.

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.25\ Na_2O\\0.15\ Na_2F_2\\0.15\ CaF_2\\0.20\ BaO\\0.15\ ZnO\end{matrix}\right\}\ \left.\begin{matrix}0.10\ Al_2O_3\\0.05\ Al_2F_6\end{matrix}\right\}\ \left.\begin{matrix}1.05\ SiO_2\\0.30\ B_2O_3\\0.05\ Sb_2O_5\\0.05\ MoO_3\end{matrix}\right.$$

Smelter batch (%)

Borax	22.5	Cryolite	8.3
Feldspar	21.9	Fluorite	4.6
Quartz	8.2	Barium carbonate	15.5
Sodium meta-antimonate	7.6	Zinc oxide	4.8
Sodium nitrate	3.4	Molybdenum trioxide (technical)	3.2
			100.0

A typical mill batch for these enamels is frit 100, clay 4 or 5, electrolyte 0.25, and water 50 parts.

VII. Summary

Not reported heretofore are the acid-resistant types of enamels for one-coat application, the raw, or partially fritted, enamels, and the new low-temperature enamels containing molybdenum trioxide smelted into the batch. The work on clear ground coats and one-coat white antimony enamels has been extended, and new compositions and a wider range of firing temperatures are reported.

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MOLYBDENUM IN ENAMELS: IV, WHITE MOLYBDENUM ENAMELS*

BY KARL KAUTZ

ABSTRACT

Compositions and characteristics of white enamels containing molybdenum in the frit are reported. The white enamels studied are the following types: (1) regular white ground coats, (2) acid-resisting white ground coats, (3) regular white finish coats for direct application to metal base, (4) acid-resisting white finish coats for direct application to the metal, and (5) acid-resisting white cover coats.

I. Introduction

In Part III of this series of papers, "Molybdenum in Enamels," there were listed a number of white molybdenum enamels for direct application to the steel base. The problem of successful white coats applied directly onto steel is a complicated one and involves not only white frits of proper composition and properties but also sheet steel of the proper composition and physical properties and carefully controlled enameling operations.

The work on white molybdenum enamels has been divided into five different groups, (1) white ground coats, ordinary, (2) white finish coats, ordinary, (3) white ground coats, acid resisting, (4) white finish coats, acid resisting, and (5) white cover coats (for overspray and second-coat applications), acid resisting.

The greatest progress has been made with the ordinary, or stainable, white enamels and with highly opaque stainless white cover-coat enamels for overspray and second coats. Stainless white coats applied directly onto steel, while showing promise, have not been fully developed.

II. Advantages of Molybdenum Enamels

Molybdenum trioxide smelted into enamels of special composition imparts to the enamel three desirable properties, (1) good adherence, (2) high opacity, and (3) low viscosity. These properties are important in compounding white enamels for direct application to steel.

Possibly because molybdic oxide melts at about 1460°F., its greatest opacifying effect is below this temperature. Enamels maturing above 1500°F. have been made successfully, but, for maximum opacity, enamels maturing between 1300°F. and 1500°F. are best. This, it is believed, results in the following advantages: (1) Sheet steels are far less reactive (oxidize less rapidly, evolve less gas, and warp less) between 1400°F. and 1500°F. than at higher temperatures; (2) furnace refractories and metallic fixtures as well as tools have a longer life at these lower temperatures; (3) less fuel is required to maintain the lower temperatures; and (4) lower firing enamels permit the use of thinner gauges of sheet steel because warping and sagging are greatly reduced.

The writer has found that enamels which have all of the desirable properties found in enamels at higher temperatures, such as acid resistance, weather resistance, high hardness, and high opacity, can be compounded in this lower range.

(1) White Molybdenum Enamels for Direct Application to Steel

(*A*) *Characteristics:* In order to coat a steel or iron sheet successfully with a vitreous enamel, the physical properties of the enamel must lie within certain limits.

A number of years ago, blue ground coats were difficult to use because of high viscosity, which often resulted in typical copperheads, blisters, or black specks; in recent years, however, these coats have been quite free of such defects, due partially to the use of enamels having lower viscosity.

Similar problems are involved in the production of white coats for direct application to steel. The typical,

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TABLE I

EFFECT OF INCREASING ELEMENT ON SOME PROPERTIES OF WHITE MOLYBDENUM ENAMEL COMPOSITIONS

Chemical element	Range used (mols)	Adherence	Viscosity	Opacity	Firing range	Color
Lithium	0–0.2	I	D	SD	SD	White
Sodium	0.3–0.8	I	D	D	D	"
Potassium	0–0.2	I	D	D	D	"
Magnesium	0–0.2	D	I	I	I	"
Calcium	0–0.3	SD	I	I	I	"
Strontium	0–0.2	SD	SI	I	I	"
Barium	0–0.3	I	SD	I	SI	"
Lead	0–0.2	D	D	SD	D	Cream
Zinc	0–0.2	SD	D	I	D	White
Aluminum	0–0.2	SD	I	I	I	"
Boron	0–0.8	I	D	D	D	
Silicon	0.6–2.0	D	I	I	I	White
Titanium	0–0.5	D	SI	I	SI	Yellow
Phosphorus	0–0.4	I	SI	I	SI	Brown
Fluorine	0–0.9	I	D	I	D	White
Oxygen	3.0–8.0					
Zirconium	0–0.2	D	I	I	I	White
Antimony	0–0.2	I	I	I	SI	"
Arsenic	0–0.1	I	SI	I	D	"
Tin	0–0.1	D	I	I	I	Cream
Molybdenum	0–0.2	I	SI	I	D	White

I, increase; D, decrease; S, slightly.

white, superopaque cover coat is very viscous, in fact almost "thermoplastic" at firing temperatures. As long as any gases are evolved from the steel base during firing, the viscous white cover-coat type of enamel cannot be used successfully as a direct coating on steel. The most successful white pigments in the past have been antimony oxide, zirconium oxide, and tin oxide, all of which greatly increase viscosity when used in amounts sufficient to produce high opacity. In some special cases, cerium oxide, titanium oxide, and arsenic oxide have been used as opacifiers, but these are of minor importance commercially.

Molybdic oxide smelted into special enamels has been found to be a very efficient opacifier; 5 to 6% in the raw batch of some enamels is sufficient to make enamels ranging between 60% and 70% in reflectance for thicknesses of 0.007 to 0.008 in. This amount of molybdic oxide increases the viscosity of the enamel to a very moderate degree; white enamels, therefore, may be compounded which fire without copperheads, blisters, or black specks.

In addition to promoting high opacity with satisfactory viscosity in enamels of special composition, molybdic oxide also acts as an adherence-promoting agent. Like cobalt and nickel oxides, it requires enamels of special composition for maximum adherence.

The special characteristics of white molybdenum enamels are (1) low viscosity, (2) high opacity, and (3) good adherence. The problem involved is to maintain these three characteristics and at the same time to develop in the enamel compositions one or more other characteristics, such as a wide firing range, color, gloss, and abrasion, sag, or acid resistance.

(*B*) *Effect of Composition on Properties:* From observations made on many white molybdenum enamels, some trends have been noted on the effect of composition on certain properties. There are many inconsistencies, and often an effect noted in one composition is absent in another; for example, small amounts of an element may have the opposite effect.

One of the most important points is the bad effect of alkalis in these enamels. Most white enamel compositions in use today are high in alkalis. This has been necessary because alkalis are known to lower viscosity, and most white cover coats have a high viscosity. In white molybdenum enamels, alkalis have been reduced to a minimum because of their deleterious effect on the opacity produced by molybdenum. In order to keep alkalis low, barium was used because it proved to be the most effective flux; in fact, barium can be used in large amounts to replace sodium with little increase in viscosity and great increase in opacity. Thus, most white molybdenum enamel compositions are of the low alkali–high barium type.

The effect of composition on the properties of white molybdenum enamels was studied by the use of molecular formulas. This method of study has proved to be quite instructive because most changes in the amount of an element could be made without affecting the molecular ratio of other elements. Only in the case of the RO content, which was maintained at unity, was it necessary to make changes by replacement. Fluorides were treated in the molecular formulas the same as oxides; thus it may be seen at a glance how fluorides are incorporated to fix the raw batch in every respect except for the ratio of soda ash to sodium nitrate.

Rather than describe in detail the specific properties imparted by each element, a table has been compiled listing the various elements used and the effect of increasing an element on some of the properties of white molybdenum enamels. In Table I, the effect of various elements on adherence, viscosity, opacity, firing range, and color are given. The words "increase" and "decrease" are used to denote the direction of the change and not the degree.

White enamels with good adherence, good opacity, and proper viscosity can be compounded with molybdic oxide as the only opacifying agent, except fluorine, in the melt. An extensive study of this type showed,

however, that it was difficult to control and that the firing range was usually narrow. Each composition had a definite molybdic oxide saturation value. When small amounts of antimony oxide were used with molybdic oxide in the batch, the saturation value of molybdic oxide in the enamel was greatly increased.

Because molybdic oxide slightly increases viscosity and antimony oxide greatly increases it, the ratio of MoO_3 to Sb_2O_3 is critical for each composition. By establishing the proper proportions of these two compounds, maximum adherence, maximum opacity, and proper viscosity can be developed.

Enamels containing zirconium oxide and molybdic oxide have also been studied. Those tried were not as satisfactory as molybdic oxide and antimony oxide. Zirconium oxide requires a very special composition to bring about its maximum opacity. Small additions of zirconium oxide and/or titanium dioxide to the molybdenum-antimony types often helped to increase gloss and surface hardness.

(*C*) *Effect of Smelting:* White molybdenum enamels are very sensitive to smelting operations and cannot stand oversmelting. The balance between molybdenum, antimony, and fluorine is critical for most compositions, and prolonged smelting or excessively high temperatures are detrimental. When smelted at 2300° to 2400°F., the loss by volatilization of some of these ingredients is so severe that adherence and opacity are adversely affected. An empirical rule is to smelt at temperatures about 600°F. higher than the designed firing temperature. Thus, in most cases, the smelting operations should be carried on between 2000°F. and 2100°F. (molten-bath temperatures). The melting-down temperatures are often higher, but the finishing temperatures should be less than 2100°F. and in some cases less than 2000°F. After the meltdown, the finishing period should be carefully observed and continued no longer than necessary. During this period, the melt should be stirred vigorously five or six times and tapped from the smelter when a cast specimen shows high gloss and freedom from pits or blisters and the string is smooth and free of lumps.

With care in duplicating temperatures and time, repeat smelts can be made which check closely.

(2) Raw Materials

The physical properties of enamels are often influenced by the choice of raw materials making up the smelter batch. The chemical composition of an enamel often may be attained by using different raw materials, although color, gloss, or opacity may be different. The complex reactions occurring during melting are affected not only by the fineness and degree of mixing but also by the choice of materials.

In the raw batches which follow, certain raw materials were used which may have had an influence on the physical properties obtained.

(1) Borax was introduced as dehydrated, or anhydrous, borax in the reported compositions; however, because hydrous borax is used quite generally in the industry, all raw batches have been calculated in terms of hydrous borax.

(2) Feldspar is reported as theoretical $K_2O \cdot Al_2O_3 \cdot 6SiO_2$ in the following batches, although the feldspar actually used had the molecular formula of $KNaO \cdot 1.15Al_2O_3 \cdot 7.5SiO_2$.

(3) Quartz was added either as powdered quartz or as silica sand.

(4) Calcium carbonate was added either as precipitated whiting or as calcspar (ground marble) with little difference in physical properties of the enamel.

(5) Barium carbonate was the dense, or heavy, variety.

(6) Zircon was used as sand rather than powdered zircon.

(7) Soda ash and soda niter were the usual commercial grades, as were cryolite, fluorspar, sodium fluosilicate, zinc oxide, titanium dioxide, and antimony oxide.

(8) Molybdenum trioxide may be obtained in two grades: (*a*) a sublimed product, which is very pure (less than 0.05% impurities), and (*b*) technical molybdenum trioxide, which varies in its content of MoO_3 from 85 to 93%.

Technical molybdenum trioxide has been found to be quite satisfactory as the source of MoO_3 for smelting into enamels; its principal impurity is silica.

The compositions which follow are reported on the basis of pure MoO_3 because the MoO_3 content of technical molybdenum trioxide varies. In compounding enamels, the proper amount of technical molybdenum trioxide to use may be obtained by multiplying the amount of pure molybdenum trioxide given in the batch by 100 and dividing by the percentage of MoO_3 in the technical molybdenum trioxide being used.

(3) Mill Additions

The white molybdenum frits were ground in the usual manner with materials commonly used in the industry. The choice of mill additions depends on the use intended.

(*A*) *Clays:* Blends of clays which promote good suspension and opacity are desirable. A wide choice of blends is on the market, and many worked successfully. For draining and slushing, 6 to 7 lb. of clay, and for spraying, 4 to 6 lb. of clay were used per 100 lb. of frit.

(*B*) *Electrolytes:* Many electrolytes were tried, the final selection being sodium nitrite, which was used generally in all enamels ground for spraying and slushing. Besides giving a good set, it prevented tearing and rusting. For ordinary enamels, $^1/_4$ lb. per 100 lb. of frit was used; for stainless enamels, the amount used was $^1/_2$ lb. per 100 lb. of frit. For draining, $^3/_4$ lb. of sodium molybdate (anhydrous) per 100 lb. of frit showed excellent results. Sodium molybdate (anhydrous) reduced set slightly and allowed drained coats of 48 to 54 gm. per sq. ft. (both sides) to be applied smoothly and uniformly.

(*C*) *Opacifiers:* The opacity of white molybdenum coats can be successfully improved by proper amounts of mill-added opacifiers. No attempt was made to study all of the various mill-added opacifiers on the market, and the mention of a certain type of opacifier

No. 1 White Ground Coat

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.30\ Na_2O\\0.10\ Na_2F_2\\0.25\ CaF_2\\0.20\ BaO\\0.05\ ZnO\end{matrix}\right\}\ \left.\begin{matrix}0.10\ Al_2O_3\\0.50\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}1.20\ SiO_2\\0.10\ SiF_4\\0.10\ MoO_3\\0.015\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	32.2	Fluorspar	6.6
Feldspar	18.7	Barium carbonate	13.3
Silica sand	12.2	Zinc oxide	1.4
Sodium nitrate	2.9	Molybdic oxide (pure)	4.8
Sodium fluosilicate	6.4	Antimony trioxide	1.5
			100.0

Finishing and pouring temp., 2050°F.

No. 2–A (Soft) White Ground Coat

Empirical formula

$$\left.\begin{matrix}0.075\ K_2O\\0.300\ Na_2O\\0.075\ Na_2F_2\\0.100\ CaF_2\\0.150\ CaO\\0.300\ BaO\end{matrix}\right\}\ \left.\begin{matrix}0.075\ Al_2O_3\\0.025\ Al_2F_6\\0.250\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}1.000\ SiO_2\\0.080\ MoO_3\\0.010\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	19.0	Fluorspar	3.1
Feldspar	16.6	Calcium carbonate	6.0
Quartz	13.2	Barium carbonate	23.5
Soda ash	5.2	Molybdic oxide (pure)	4.6
Sodium nitrate	3.4	Antimony trioxide	1.2
Cryolite	4.2		
			100.0

Finishing and pouring temp., 2000°F.

No. 2–B (Hard) White Ground Coat

Empirical formula

$$\left.\begin{matrix}0.100\ K_2O\\0.350\ Na_2O\\0.100\ Na_2F_2\\0.200\ CaO\\0.250\ BaO\end{matrix}\right\}\ \left.\begin{matrix}0.100\ Al_2O_3\\0.400\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}1.50\ SiO_2\\0.10\ SiF_4\\0.11\ MoO_3\\0.012\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	24.5	Sodium fluosilicate	6.0
Feldspar	17.7	Calcium carbonate	6.4
Quartz	17.3	Barium carbonate	15.7
Soda ash	3.4	Molybdic oxide (pure)	5.1
Sodium nitrate	2.7	Antimony trioxide	1.2
			100.0

Finishing and pouring temp., 2100°F.

in the mill batch does not mean that other opacifiers cannot be used. For coatings directly on steel, the zirconium opacifiers gave good results; for stainless cover coats, the calcium-antimony-titanium opacifiers gave good results.

(4) White Ground Coats, Ordinary

The compositions listed as white ground coats have been used as prime or grip coats directly on steel. They are characterized by poor gloss and surface texture in many cases, which eliminate them for one-fire white finishes. They have excellent adherence over quite a range of temperature and some compositions are quite opaque. Second coats of stainable white cover enamel or stainless white cover enamel may be applied without difficulty. One-fire, white finishes may be made by overspraying these white ground coats with a light

No. 3–A (Soft) White Ground Coat

Empirical formula

$$\left.\begin{matrix}0.050\ K_2O\\0.425\ Na_2O\\0.075\ Na_2F_2\\0.150\ CaF_2\\0.300\ BaO\end{matrix}\right\}\ \left.\begin{matrix}0.050\ Al_2O_3\\0.025\ Al_2F_6\\0.250\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}1.000\ SiO_2\\0.08\ MoO_3\\0.01\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	19.1	Cryolite	4.2
Feldspar	11.0	Fluorspar	4.6
Quartz	16.6	Barium carbonate	23.3
Soda ash	8.4	Molybdic oxide (pure)	4.3
Sodium nitrate	7.3	Antimony trioxide	1.2
			100.0

Finishing and pouring temp., 1950°F.

No. 3–B (Hard) White Ground Coat

Empirical formula

$$\left.\begin{matrix}0.100\ K_2O\\0.350\ Na_2O\\0.100\ Na_2F\\0.150\ CaF_2\\0.300\ BaO\end{matrix}\right\}\ \left.\begin{matrix}0.100\ Al_2O_3\\0.400\ B_2O_3\end{matrix}\right\}\ \left\{\begin{matrix}1.50\ SiO_2\\0.10\ SiF_4\\0.10\ MoO_3\\0.012\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	24.5	Sodium fluosilicate	6.1
Feldspar	17.9	Fluorspar	3.7
Quartz	17.1	Barium carbonate	19.0
Soda ash	3.3	Molybdic oxide (pure)	4.5
Sodium nitrate	2.7	Antimony trioxide	1.1
			100.0

Finishing and pouring temp., 2100°F.

coating of white cover coat, either stainable or stainless.

The composition of a single-frit, white ground coat is given under No. 1. This frit has excellent adherence between 1400°F. and 1550°F. The opacity decreases with increase in temperature and the enamel is slightly overfired at 1550°F. Its best firing range is between 1450°F. and 1500°F. The other frit compositions given are for two-frit, or twin-frit, ground coats; No. 2–A is a low-maturing frit and No. 2–B is high maturing. These can be blended in almost any proportion to give a series of white ground coats which mature from 1350° to 1550°F.; Nos. 3–A and 3–B, likewise, are for two-frit white ground coats and can be used in any proportions; No. 3–A is exceptionally low maturing, having excellent adherence at 1300°F. and possibilities as a one-fire, white finish coat between 1300°F. and 1400°F., especially on very light-gauge sheet steel. It will be mentioned again under white finish coats, acid resisting.

For coats applied by draining, the following mill batch gave good results: Frits (A plus B) 100, clay 6, sodium molybdate (anhydrous) 0.75, zirconium opacifier 4, and water 40 parts; grinding, 4 gm. on 200-mesh, 50 cc.; application, 48 to 54 gm. per sq. ft. (both surfaces).

For coats applied by spraying, the following mill batch gave good results: Frits (A plus B) 100, clay 6, sodium nitrite 0.25, zirconium opacifier 4, and water 45 parts; grinding, 1 gm. on 200-mesh, 50 cc.; application, 30 to 40 gm. per sq. ft. by spraying (single surface); firing, 1400° to 1500°F., 4 minutes, according to the blend used.

No. 4 White Finish Coat, Ordinary

Empirical formula

$$\left.\begin{matrix}0.075\ K_2O\\0.375\ Na_2O\\0.250\ CaF_2\\0.300\ BaO\end{matrix}\right\}\ 0.075\ Al_2O_3\ \left\{\begin{matrix}1.000\ SiO_2\\0.070\ MoO_3\\0.020\ Sb_2O_3\end{matrix}\right.$$
$$0.250\ B_2O_3$$

Smelter batch (%)

Borax (hydrous)	19.0	Fluorspar	7.8
Feldspar	16.6	Barium carbonate	23.6
Quartz	13.1	Molybdic oxide (pure)	4.0
Soda ash	6.3	Antimony trioxide	2.3
Soda niter	7.3		
			100.0

Finishing and pouring temp., 1950°F.; firing temp., 1350° to 1500°F.

No. 5 White Finish Coat, Ordinary

Empirical formula

$$\left.\begin{matrix}0.050\ K_2O\\0.375\ Na_2O\\0.075\ Na_2F_2\\0.200\ CaF_2\\0.250\ BaO\\0.050\ ZnO\end{matrix}\right\}\ \begin{matrix}0.050\ Al_2O_3\\0.025\ Al_2F_6\\0.250\ B_2O_3\end{matrix}\ \left\{\begin{matrix}1.000\ SiO_2\\0.075\ MoO_3\\0.015\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	20.0	Fluorspar	6.4
Feldspar	11.5	Barium carbonate	20.3
Quartz	17.4	Zinc oxide	1.6
Soda ash	8.7	Molybdic oxide (pure)	4.4
Soda niter	3.5	Antimony trioxide	1.8
Cryolite	4.4		
			100.0

Finishing and pouring temp., 2000°F.; firing temp., 1350° to 1500°F.

(5) White Finish Coats, Ordinary

There is little difference in composition between white ground coats and white finish coats, and in some cases they are interchangeable. The white finish coats represent attempts to produce high gloss and good surface texture in addition to the characteristics noted for white ground coats. Higher opacity is also desirable so that single coats of 30 to 40 gm. per sq. ft. applied directly on the steel will suffice for a finished product. No specific rule can be given which will convert a white ground coat to a white finish coat. They are produced with minor changes in composition and careful smelting.

All of the white finish coats are one-frit compositions because high gloss and good surface texture can be developed in a single frit much more easily than in two-frit combinations. Blends of two or more frits quite often give poor gloss and surface texture.

While one-fire, white finish coats can be successfully made under carefully controlled conditions, the complete commercial success of this coating will depend to a great extent on the sheet steel used and operations in the enameling plant. Localized evolution of gases from the steel or oxidation spots due to faulty cleaning methods will produce defects sufficient to reject an otherwise acceptable surface. It is believed, however, that one-fire, white finish coats can be attempted commercially with present-day sheet steels. As sheet steels and enameling operations are improved so will the yield of one-fire, white finish coats increase.

No. 6 White Finish Coat, Ordinar

Empirical formula

$$\left.\begin{matrix}0.115\ K_2O\\0.231\ Na_2O\\0.085\ Na_2F_2\\0.170\ CaF_2\\0.114\ CaO\\0.285\ BaO\end{matrix}\right\}\ \begin{matrix}0.115\ Al_2O_3\\0.028\ Al_2F_6\\0.400\ B_2O_3\end{matrix}\ \left\{\begin{matrix}1.200\ SiO_2\\0.095\ MoO_3\\0.011\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	26.6	Fluorspar	4.6
Feldspar	22.2	Calcspar	4.0
Quartz	10.6	Barium carbonate	19.5
Sodium nitrate	1.8	Molybdic oxide (pure)	5.4
Cryolite	4.1	Antimony trioxide	1.2
			100.0

Finishing and pouring temp., 2050°F.; firing temp., 1425° to 1525°F.

No. 7 White Finish Coat, Ordinary

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.25\ Na_2O\\0.10\ Na_2F_2\\0.15\ CaF_2\\0.10\ CaO\\0.25\ BaO\\0.05\ ZnO\end{matrix}\right\}\ \begin{matrix}0.10\ Al_2O_3\\0.033\ Al_2F_6\\0.40\ B_2O_3\end{matrix}\ \left\{\begin{matrix}1.20\ SiO_2\\0.05\ TiO_2\\0.08\ MoO_3\\0.02\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	26.5	Calcspar	3.5
Feldspar	19.3	Barium carbonate	17.2
Quartz	12.6	Zinc oxide	1.4
Sodium nitrate	3.0	Titanium dioxide	1.4
Cryolite	4.9	Molybdic oxide (pure)	4.1
Fluorspar	4.1	Antimony trioxide	2.0
			100.0

Finishing and pouring temp., 2100°F.; firing temp., 1425° to 1525°F.

Four white enamels have been selected, from the many studied, to represent the range in composition of ordinary white finish coats (Nos. 4, 5, 6, and 7).

For coats applied by spraying, the following mill batch was standard for all one-fire white finish coats: Frit 100, clay 6, sodium nitrite 0.25, zirconium opacifier 4, and water 45 parts; grinding, 1 gm. on 200-mesh, 50 cc.; application, 40 gm. per sq. ft. (single surface) by spraying; best firing, 1425°F., 4 minutes, for Nos. 4 and 5 and 1475°F., 4 minutes, for Nos. 6 and 7.

(6) White Ground Coats, Acid Resisting

The development of acid-resisting, white ground coats has not progressed as far as ordinary white ground coats. Enough work has been done, however, to predict that this type of coating can be made successfully although it may not be as workable as the ordinary white ground coat.

Two compositions are given. Neither is completely stainless. They are both slightly stained with 10% citric acid but are not etched, that is, they pass the wet rubbing test for class B. These enamels do not have high opacity (60% reflectance per 40-gm. coat) and the firing range is narrow. They are shown because they represent the progress made in this direction at the time of this report.

No. 8 White Ground Coat, Semiacid Resisting

Empirical formula

$$\left.\begin{matrix}0.50\ Na_2O\\0.20\ CaF_2\\0.25\ BaO\\0.05\ ZnO\end{matrix}\right\}\ 0.25\ B_2O_3\ \left\{\begin{matrix}1.00\ SiO_2\\0.25\ TiO_2\\0.075\ MoO_3\\0.025\ Sb_2O_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	18.2	Barium carbonate	19.0
Silica sand	23.0	Zinc oxide	1.5
Soda ash	11.2	Titanium dioxide	7.6
Soda niter	6.5	Molybdic oxide (pure)	4.2
Fluorspar	6.0	Antimony trioxide	2.8
			100.0

Finishing and pouring temp., 2050°F.; firing temp., 1450° to 1550°F.

No. 9 White Ground Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.60\ Na_2O\\0.05\ Na_2F_2\\0.25\ ZnO\\0.10\ CaO\end{matrix}\right\}\ 0.016\ Al_2F_6\ \left\{\begin{matrix}1.00\ SiO_2\\0.125\ TiO_2\\0.033\ P_2O_5\\0.05\ Sb_2O_3\\0.10\ MoO_3\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	10.4	Zinc oxide	9.0
Silica sand	27.0	Calcium phosphate	4.6
Soda ash	20.8	Titanium dioxide	4.5
Soda niter	7.6	Molybdic oxide (pure)	6.5
Cryolite	3.1	Antimony trioxide	6.5
			100.0

Finishing and pouring temp., 2100°F.; firing temp., 1450° to 1550°F.

The acid-resisting white ground coat could have many applications in the architectural, sanitary, and utensil field, both as a base for second acid-resisting coats and as a single coat for white and light colors, or acid-resisting oversprays in one fire.

Much work remains to be done, however, before satisfactory commercial results can be expected.

The two compositions which follow are believed to be steps in the right direction, although they do not possess all of the characteristics at present required.

For coats applied by spraying, the following mill batch was used: Frit 100, clay 5, sodium nitrite 0.5, antimony opacifier 4, and water 40 parts; grinding, 1 gm. on 200-mesh, 50 cc.; application, 30 to 40 gm. per sq. ft. (single surface) by spraying; and best firing, 1475°F., 4 minutes.

(7) White Finish Coats, Acid-Resisting

The ultimate goal of the enameler is the acid-resisting white finish coat directly on steel. Such a coating, if endowed with the proper characteristics of color, gloss, and high opacity, in addition to acid resistance, would indeed have almost unlimited possibilities. It is, however, the most difficult composition to develop because of many complexities involved. Stainless enamels usually are high in SiO_2, which results in high viscosities and blistering of the enamel coating when applied directly to steels. The use of TiO_2 permits a reduction of SiO_2 to some extent, but the best stainless enamels remain in the disilicate range ($RO \cdot 2SiO_2$). The most workable white molybdenum ground coats and finish coats are in the metasilicate range ($RO \cdot SiO_2$). Attempts to lower the $RO:SiO_2$ ratio from 1:2 to 1:1 have been attended by loss of acid resistance or poor color or both. The acid-resisting white ground coats just reported show that semiacid-resisting enamels in the metasilicate range are possible although color is often unfavorable.

The problem of acid-resisting white finish coats on steel has been attacked in three ways: (*A*) low maturing white molybdenum frits with large mill additions of TiO_2, (*B*) aluminophosphate enamels (silica-free), and (*C*) titano-silicate enamels. Each of these three types of enamels has shown promising results, but obstacles have been encountered in each which have not yet been entirely overcome.

(*A*) An example of the low-maturing white molybdenum frit is No. 3–A, reported under white ground coats, ordinary. The following mill batch was used: Frit No. 3–A 100, clay 5, sodium nitrite 0.25, titania 20, and water 65 parts. When this batch was ground extremely fine, it gave excellent adherence at between 1300°F. and 1400°F., with reflectance readings of 72 to 64% and acid resistance just short of class A. Partial solution of TiO_2 in the frit, however, occurred with a mottled appearance and poor gloss. Titanium dioxide cannot be used as a mill addition above 1400°F. in this type of frit because of the cream and yellow colors developed. The yellow color increased and gloss decreased with increase of firing temperature. Titanium dioxide undergoes allotropic changes with increase of temperature, resulting in the crystalline phases, anatase → brookite → rutile. Anatase is white, brookite is yellow, and rutile is brown. If TiO_2 could be stabilized in the anatase form so that firing temperatures up to 1500°F. could be used, this method would be quite promising; TiO_2 also affects gloss and produces high set in the milled enamel. Another frit similar to No. 3–A but containing 3.5% TiO_2 in the smelter batch gave, when milled with 30 parts of TiO_2, excellent adherence at 1350°F., class A acid resistance, and 72% reflectance for a thickness of 0.004 in.

(*B*) A new type of glass which shows promise for low-maturing stainless enamels is the silica-free, aluminophosphate-type enamel. This enamel is characterized by high alumina and high phosphorus pentoxide, with alkalis and zinc oxide as RO. Alkaline earths, such as CaO and BaO, cannot be used in this type of enamel because of brown colors and insoluble compounds separating during smelting. Because P_2O_5 is extremely high, it cannot be introduced wholly as sodium phosphates. Phosphoric acid cannot be used because it does not fit into dry-mixing methods used in smelting. Monoammonium orthophosphate was found to be ideal for introducing P_2O_5, because, during smelting, H_2O and NH_3 were evolved, leaving P_2O_5 in the glass. Monoammonium orthophosphate has the chemical formula of $NH_4H_2PO_4$, or $(NH_4)_2O \cdot 2H_2O \cdot P_2O_5$, and a molecular weight of 230 for each mol of P_2O_5. Alumina is introduced as alumina hydrate, or as cryolite, and the alkalis as potassium nitrate, potassium carbonate, and sodium carbonate. The

cost of such an enamel is greater than the silicate type, but workable, stainless white enamels in one-fire use would justify its greater cost. These enamels have high gloss, high surface hardness, and are completely stainless with citric acid. Molybdic oxide cannot be smelted into these enamels because of the yellow-brown colors developed, due, probably, to the formation of yellow phosphomolybdates. Antimony oxide likewise gives gray colors and must be used sparingly. Zirconium oxide, ZrO_2, has been found to be a very good opacifier and gives good whites, but its adherence is nil; however, by using $BaMoO_4$ and Sb_2O_3 as mill additions, good adherence may be obtained with the zirconium oxide-opacified aluminophosphate frits.

A typical example of the low-maturing, stainless, white aluminophosphate enamel is No. 10.

No. 10 White Finish Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.20\ K_2O\\0.45\ Na_2O\\0.15\ Na_2F_2\\0.20\ ZnO\end{matrix}\right\}\ \begin{matrix}0.50\ Al_2O_3\\0.05\ Al_2F_6\\0.30\ B_2O_3\end{matrix}\ \left\{\begin{matrix}0.75\ P_2O_5\\0.20\ ZrO_2\end{matrix}\right.$$

Smelter batch (%)

Potassium nitrate	4.6	Zinc oxide	3.7
Potassium carbonate	3.2	Alumina hydrate	17.9
Borax (hydrous)	13.2	Monoammonium orthophosphate	39.6
Sodium carbonate	7.3	Zirconium oxide	5.7
Cryolite	4.8		
			100.0

Finishing and pouring temp., 1900°F.; firing temp., 1300° to 1400°F.

For coats applied by spraying, the following mill batch gave good results: Frit 100, clay 4, sodium nitrite 0.5, zirconium opacifier 4, barium molybdate 1.5, antimony oxide 1.5, and water 45 parts; grinding, 1 gm. on 200-mesh, 50 cc.; application, 30 to 40 gm. per sq. ft. (single surface) by spraying; and best firing, 1350°F., 4 minutes.

(*C*) The titano-silicate type of enamel is familiar to most enamelers. This is the type commonly used for white, acid-resisting cover coats. Two examples are given, one with fluorine and the other fluorine free. Both are of the disilicate type, that is, the ratio of $RO:SiO_2$ is 1:2. The viscosity of this type of enamel is higher than it should be for consistently good results with gas-evolving steels.

These enamels show slight staining but no etching. They have a tendency to blister on some steels and the firing range is narrow.

For coats applied by spraying, the following mill batch was used: frit 100, clay 4, sodium nitrite 0.5, zirconium opacifier 4, and water 40 parts; grinding, 1 gm. on 200-mesh, 50 cc.; application, 40 gm. per sq. ft. (single surface) by spraying; best firing, 1500°F., 4 minutes.

(8) White Cover Coats, Acid Resisting

The acid-resisting, white cover coats which follow are modifications of this type of enamel so that they could be used as oversprays over white ground coats and white finish coats, or as second coats, within the firing range of 1350° to 1500°F. Many of the commercial, acid-resisting, white cover coats tried experimentally for this purpose were unsatisfactory because of their high viscosity, high maturing temperatures, and tendency to react with the white molybdenum undercoat. The compositions reported have been used experimentally as oversprays with fair success because they have low maturing temperatures, medium viscosities, high opacities, and do not react with the undercoat. Some are quite stainless; others show slight staining. Opacities are lower in the stainless type than in the slight staining type and range from 62 to 66% reflectance to 68 to 72% for the latter for a 40-gm. coat. They have molybdic oxide smelted into

No. 11 White Finish Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.40\ Na_2O\\0.10\ Na_2F_2\\0.10\ CaO\\0.30\ BaO\end{matrix}\right\}\ 0.35\ B_2O_3\ \left\{\begin{matrix}2.10\ SiO_2\\0.10\ SiF_4\\0.30\ TiO_2\\0.10\ MoO_3\\0.02\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	18.0	Whiting	2.8
Silica sand	34.0	Barium carbonate	16.0
Potassium nitrate	5.5	Titanium dioxide	6.5
Soda ash	6.5	Molybdic oxide (pure)	4.0
Sodium fluosilicate	5.2	Antimony trioxide	1.5
			100.0

Finishing and pouring temp., 2100°F.; firing temp. 1450° to 1550°F.

No. 12 White Finish Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.60\ Na_2O\\0.10\ CaO\\0.30\ BaO\end{matrix}\right\}\ 0.25\ B_2O_3\ \left\{\begin{matrix}2.00\ SiO_2\\0.20\ TiO_2\\0.10\ MoO_3\\0.02\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	14.4	Barium carbonate	18.0
Silica sand	36.3	Titanium dioxide	5.0
Soda ash	12.0	Molybdic oxide (pure)	4.4
Sodium nitrate	5.2	Antimony trioxide	1.7
Whiting	3.0		
			100.0

Finishing and pouring temp., 2150°F.; firing temp., 1450° to 1550°F.

Three compositions are reported; No. 13 is stainless and Nos. 14 and 15 show very slight staining.

No. 13 White Cover Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.65\ Na_2O\\0.05\ Na_2F_2\\0.15\ CaO\\0.15\ ZnO\end{matrix}\right\}\ 0.30\ B_2O_3\ \left\{\begin{matrix}2.05\ SiO_2\\0.05\ SiF_4\\0.20\ TiO_2\\0.10\ MoO_3\\0.10\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	17.2	Whiting	4.5
Silica sand	37.2	Zinc oxide	3.7
Soda ash	11.1	Titanium dioxide	4.8
Soda niter	2.6	Molybdic oxide (pure)	4.4
Sodium fluosilicate	2.9	Sodium antimonate	11.6
			100.0

Smelting and pouring temp., 2100°F.; firing temp., 1350° to 1500°F.

No. 14 White Cover Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.50\ Na_2O\\0.10\ Na_2F_2\\0.15\ CaO\\0.10\ BaO\\0.15\ ZnO\end{matrix}\right\}\ 0.40\ B_2O_3\ \left\{\begin{matrix}1.90\ SiO_2\\0.10\ SiF_4\\0.20\ TiO_2\\0.10\ MoO_3\\0.10\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	21.2	Barium carbonate	5.5
Silica sand	31.6	Zinc oxide	3.3
Soda ash	7.4	Titanium dioxide	4.5
Soda niter	2.4	Molybdic oxide (pure)	4.0
Sodium fluosilicate	5.2	Sodium antimonate	10.7
Whiting	4.2		
			100.0

Finishing and pouring temp., 2100°F.; firing temp., 1350° to 1500°F.

No. 15 White Cover Coat, Acid Resisting

Empirical formula

$$\left.\begin{matrix}0.10\ K_2O\\0.40\ Na_2O\\0.10\ Na_2F_2\\0.10\ CaF_2\\0.15\ BaO\\0.15\ ZnO\end{matrix}\right\}\ 0.40\ B_2O_3\ \left\{\begin{matrix}1.90\ SiO_2\\0.10\ SiF_4\\0.20\ TiO_2\\0.10\ MoO_3\\0.10\ Sb_2O_5\end{matrix}\right.$$

Smelter batch (%)

Borax (hydrous)	21.3	Barium carbonate	8.3
Silica sand	31.8	Zinc oxide	3.4
Soda ash	2.9	Titanium dioxide	4.5
Potassium nitrate	5.5	Molybdic oxide (pure)	4.0
Sodium fluosilicate	5.3	Sodium antimonate	10.8
Fluorspar	2.2		
			100.0

Finishing and pouring temp., 2100°F.; firing temp., 1350° to 1500°F.

them, not for adherence but to increase opacity and lower surface tension. When using molybdic oxide in the smelt, titanium dioxide must be reduced to a minimum because yellow or brown colors occur when the titanium dioxide content is high.

The use of these acid-resisting white cover coats as second coats presents no difficulties. They may be applied in any thickness from 0.002 to 0.008 in. and fired at the same time and temperature as white ground coats. As oversprays, 20- to 30-gm. coatings of white ground coat are applied by spraying followed immediately by sprayed coatings of 15 to 25 gm. of the acid-resisting, white cover coat. Considerable care is required in spraying to prevent mixing or penetration of the two dissimilar coatings.

For coats applied by spraying, the following mill batch was used: frit 100, clay 4, sodium nitrite 0.5, antimony opacifier 4, and water 40 parts; grinding, 1 gm. on 200-mesh, 50 cc.; application, 15 to 30 gm. per sq. ft. (single surface) as an overspray or second coat; best firing range, 1400° to 1500°F.

III. Summary

The research and development work reported here has been limited to white molybdenum enamels. One-fire, light-colored enamels may be made by milling the proper colored pigment with the white molybdenum frits reported.

In review, the most practical applications of these enamels may be listed in the following order: (1) white ground coats with oversprays or second coats of acid-resisting, white cover enamel; (2) white finish coats as one-fire finishes (white or colored); (3) acid-resisting, white ground coats with oversprays or second coats of acid-resisting white cover enamel; and (4) acid-resisting white ground coats as one-fire finishes (white or colored).

The enamels of group (1) should find their greatest use in the home appliance and utensil fields. The white finish coats, group (2), show promise of meeting lacquer competition for home appliances if properly developed. The sanitary field desires enamels "acid resisting all the way to the base" and should benefit by properly developed enamels of group (3), while architectural finishes should be developed principally with group (4) enamels.

It should be stressed again that the acid-resisting white enamels for direct application have not been fully developed at this time, and the satisfactory utilization of these enamels awaits further research and development work.

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SOME CLAY-WATER PROPERTIES OF CERTAIN CLAY MINERALS*

By R. E. Grim and F. L. Cuthbert†

Abstract

Computed values are given for the thickness of the water film adsorbed on the surfaces of the various clay minerals when clays composed of such minerals develop specific plastic characteristics. Based on such values, the following concept of clay-water relationships is presented: The dominant factor determining the plastic properties of clays is the rigidity of the water held on the surfaces of the clay minerals, and the point of beginning of the transition of completely rigid water to liquid water is marked by great changes in such properties. Each type of clay mineral seems to have a characteristic ability to stabilize water, and the exchangeable ions also exert an influence. The reaction between water and kaolinite or halloysite may require considerable time so that there is frequently a time lag after mixing clays composed of such minerals before the plastic properties are fully developed.

Applications of the foregoing concept in the fields of geology, ceramics, and soil mechanics are suggested.

I. Introduction

In the course of an investigation of the constitution and bonding and related properties of clays for metallurgical use under the sponsorship of the Illinois State Geological Survey, the Department of Mechanical Engineering of the University of Illinois, and the Illinois Clay Products Company, Joliet, Illinois, a fundamental study was made of the bonding characteristics (as shown in molding sands) of types of clay based on their clay-mineral composition. In addition to information regarding the bonding properties of clays, the study has provided some data on general clay-water relationships that seem to have broad applications in industry, engineering, and science. It is the purpose of this paper to present these findings regarding the general clay-water relationship together with the experimental data that support them and a discussion of their application. The detailed results of the study as they pertain to bonding clays and molding sands are being published elsewhere.[1]

II. Thickness of Water with a Definite Configuration Adsorbed on Basal Plane Surfaces of Montmorillonite

When the compression strength is determined for rammed specimens of sand-clay mixtures that contain various amounts of tempering water, results similar to those shown in Fig. 1 are obtained. In such curves, the tempering water is shown in percentage of total weight of the sand-clay mixture. Figure 1, (*A*) and (*B*), shows a group of curves for a series of mixtures with varying amounts (*A*) of sodium-montmorillonite clay and (*B*) of calcium-montmorillonite clay. The data on which these clay-mineral identifications are based are being published elsewhere.[1] It is obvious from the curves that the maximum strength of the sand-clay mixture or the maximum bonding power of the clay is developed for each mixture when there is a precise and narrowly limited amount of tempering water present.

Table I

Water-Film Thickness per Unit Cell of Montmorillonite at Maximum Green Compression Strength

	Sodium-montmorillonite clay			Calcium-montmorillonite clay		
Clay in mixture (%)	Dry (110°C.) wt. of clay (gm.)*	Water (cc.)*	Water-film thickness in molecular layers†	Dry (110°C.) wt. of clay (gm.)*	Water (cc.)*	Water-film thickness in molecular layers†
6	111	33	3	111	45	4
7	129	37	3			
8	147	42	3	147	54	4
9	156	48	3			
10	184	52	3	184	64	3+
12	222	66	3	222	77	3+
15	277	83	3	277	94	3+

* These values are based on a 2000-gm. mixture: dry weight (110°C.) of clay is less than the percentage value because of water loss from room temperature to 110°C.

† A single layer of water one molecule thick per unit cell of montmorillonite is equal to 0.1 gm. of water per gm. of clay if it is assumed that the water has the loose packing required by the configuration of Hendricks and Jefferson (footnote 2(*a*)).

Table I shows the thickness of the water on each unit flake of montmorillonite when there is just enough water to produce the maximum green strength shown in Fig. 1. These computations are based on the assumption that all basal plane surfaces of units of montmorillonite are available to the penetration of water and the development of water layers. This assumption

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[1] R. E. Grim and F. L. Cuthbert, "Bonding Action of Clays: I, Clays in Green Molding Sands," *Illinois Geol. Survey Rept. Invest.*, No. 102 (in press); *Univ. of Illinois Eng. Expt. Sta. Bull.*, No. 357 (in press); "II, Clays in Dry Molding Sands" (manuscript in preparation).

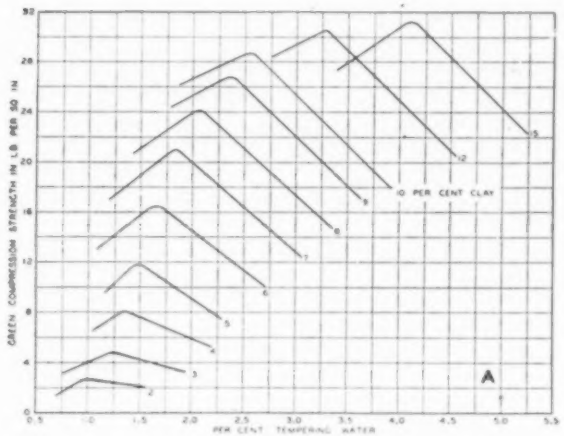

FIG. 1 (*A*).—Relation of compression strength to tempering water for sand-clay mixtures containing various amounts of sodium-montmorillonite clay.

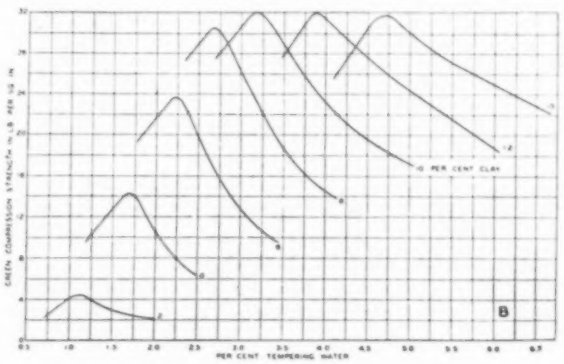

FIG. 1 (*B*).—Relation of compression strength to tempering water for sand-clay mixtures containing various amounts of calcium-montmorillonite clay.

is valid since it is well known that montmorillonite tends to break down in the presence of water to unit cell size.

The computations show the striking result that, regardless of the amount of clay, the maximum bonding strength is developed in the sodium-montmorillonite clay when there is just enough water to coat each basal surface with a water layer four molecules thick.

Recently it has been rather well established that the water[2] held on the basal surfaces of flakes of montmorillonite is made up of water molecules that tend to be arranged in a definite pattern. The water is, therefore, in a rigid condition rather than fluid. The configuration of the water molecules is determined largely by the arrangement of oxygen atoms in the surface layers of the montmorillonite, and, as a consequence, should extend to a limited distance from the montmorillonite surface.

[2] (*a*) S. B. Hendricks and M. E. Jefferson, "Structures of Kaolin and Talc-Pyrophyllite Hydrates and Their Bearing on Water Sorption of Clays," *Amer. Mineralogist*, **23** [12] 863–75 (1938); *Ceram. Abs.*, **18** [4] 113 (1939).
(*b*) R. E. Grim, "Modern Concepts of Clay Materials," *Jour. Geol.*, **50** [3] 225–75 (1942); *Ill. Geol. Survey Rept. Investigation*, No. 80 (1942); *Ceram. Abs.*, **21** [8] 177 (1942).

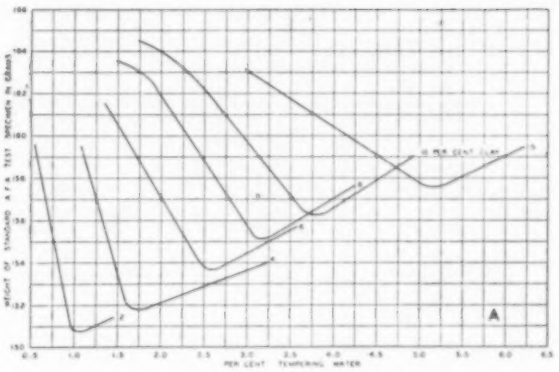

FIG. 2 (*A*).—Relation of bulk density to tempering water for sand-clay mixtures containing various amounts of sodium-montmorillonite clay.

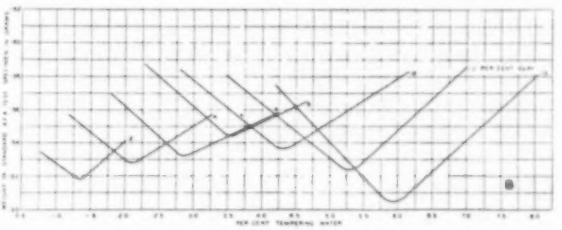

FIG. 2 (*B*).—Relation of bulk density to tempering water for sand-clay mixtures containing various amounts of calcium-montmorillonite clay.

The concept has been developed elsewhere[1] that maximum green compression strength in sand-clay-water mixtures develops when the clay-water component has the maximum thickness and maximum degree of rigidity for a given clay content. If this be true and molding-sand characteristics provide a considerable body of supporting evidence, then the tempering water at maximum green compression strength is a measure of the maximum amount of water that can be held with the water molecules in about perfect orientation. The sodium montmorillonite retains about completely oriented water molecules to a thickness of 3 molecules (about 9 a.u.) on each basal unit surface and calcium montmorillonite to a thickness of 4 molecules (about 12 a.u.) on each basal unit surface.

If the bulk density is determined for a sand-clay-water mixture that has been rammed in a mold and if such bulk density values are plotted against variations in amount of tempering water, curves such as those shown in Fig. 2, (*A*) and (*B*), will be obtained. These figures show that for each proportion of sand and clay there is a precise, and narrowly limited, amount of water wherein minimum bulk density is developed. Minimum bulk density develops at that moisture content which gives the mixture the greatest resistance to packing during the ramming in a mold.[1]

Table II gives computed values of the thickness of the layer of water on each unit flake of montmorillonite

TABLE II

WATER-FILM THICKNESS PER UNIT CELL OF MONTMORILLONITE AT MINIMUM BULK DENSITY

	Sodium-montmorillonite clay			Calcium-montmorillonite clay		
Clay in mixture (%)	Dry (110°C.) wt. of clay (gm.)*	Water (cc.)*	Water-film thickness in molecular layers	Dry (110°C.) wt. of clay (gm.)*	Water (cc.)*	Water-film thickness in molecular layers
6	111	52	4+	111	57	5
8	147	63	4+	147	71	5
10	184	76	4	184	86	5−
12				222	106	5−
15	277	103	4−	277	119	4+

* Values based on 2000-gm. mixture.

when there is just enough water to permit the greatest resistance to packing, that is, at the point of minimum bulk density. Again it is assumed that each basal plane surface of montmorillonite is available to water penetration. The computation shows that for the sodium montmorillonite this condition is reached when water is present equal to a layer 4 molecules thick (about 12 a.u.) and for the calcium montmorillonite when water is present equal to a layer 5 molecules thick (about 15 a.u.). In other words, for each of these two montmorillonite clays an extra molecular water layer above those that are held with maximum rigidity is necessary to develop maximum resistance to packing.

It seems logical that maximum resistance to packing would prevail not when the clay-water coating of the quartz grains is completely rigid but when there is a certain adherence between the coatings of the grains, such as would occur in the presence of some incompletely rigid (but not liquid) water. It seems likely, therefore, that the addition of a single layer of water above that amount held completely rigid provides water in which the water molecules are not perfectly oriented. That is, beyond a layer 3 water molecules thick for sodium montmorillonite, and 4 water molecules thick for calcium montmorillonite, the perfection of the orientation of the water molecules is reduced but not destroyed completely. It seems clear that the perfection of orientation of the water molecules adsorbed by these montmorillonites decreases gradually rather than abruptly for thicknesses greater than 3 or 4 molecules, respectively.

The data indicate that the thickness of completely rigid water is greater when calcium rather than sodium is the exchangeable base. This does not mean that the total thickness of water that can be held with any degree of orientation of the water molecules is greater for calcium than for sodium. In fact, the well-known thixotropic properties of water suspensions of sodium-montmorillonite clays and other data from molding-sand studies suggest that the reverse is true.

The reason for the thicker coating of completely rigid water when calcium is the chief exchangeable base is not definitely known, but it is probably related to the fact that the calcium ion hydrates whereas the

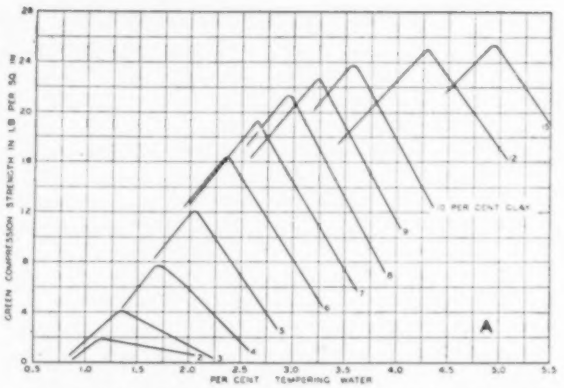

FIG. 3 (*A*).—Sand-clay mixtures containing halloysite clay showing relation of compression strength to tempering water.

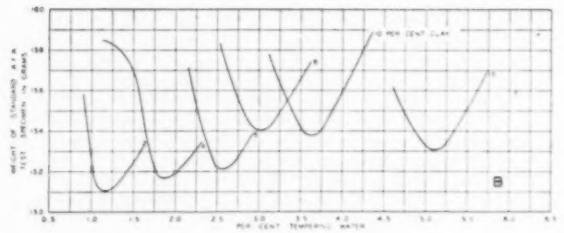

FIG. 3 (*B*).—Sand-clay mixtures containing halloysite clay showing relation of tempering water to bulk density.

sodium ion does not.[3] The exchangeable ions are held close to or at the surface of the montmorillonite flakes, and the hydration of the calcium ion might well be an additional force tending to develop configuration in the water molecules (the main force being the orientation of the oxygen atoms in the basal surface of the montmorillonite itself). Other factors, such as the force tending to hold the montmorillonite flakes together,[2(b)] probably largely control the total thickness of water that can develop with any definite configuration, so it does not follow from this reasoning that, when calcium ions are present, the water layer with any degree of configuration of the molecules should be thickest.

There is no basis for computing the thickness of the adsorbed water film in clays composed of other clay minerals because water does not penetrate readily between each individual layer. As shown in Figs. 3, 4, and 5, curves for halloysite, kaolinite, and illite clays, representing the relation of tempering water to green compression strength and to minimum bulk density, have the same general shape as those for montmorillonite clays. From this fact and other considerations of the bonding properties of these clays (for example, air-set strength, see section IV), it seems certain that water in which there is a definite configuration of the molecules develops on the available plane surfaces of these clay minerals.

[3] S. B. Hendricks, R. A. Nelson, and L. T. Alexander, "Hydration Mechanism of the Clay Mineral Montmorillonite Saturated with Various Cations," *Jour. Amer. Chem. Soc.*, **62** [6] 1457–64 (1940); *Ceram. Abs.*, **19** [11] 265 (1940).

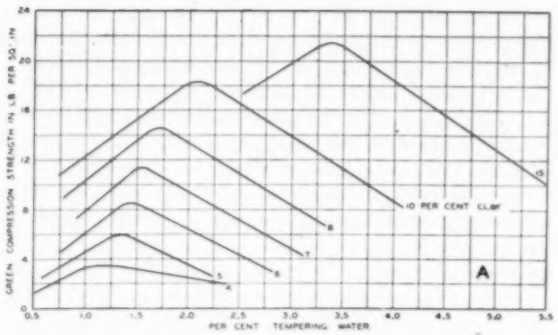

FIG. 4 (*A*).—Sand-clay mixtures containing kaolinite clay showing relation of compression strength to tempering water.

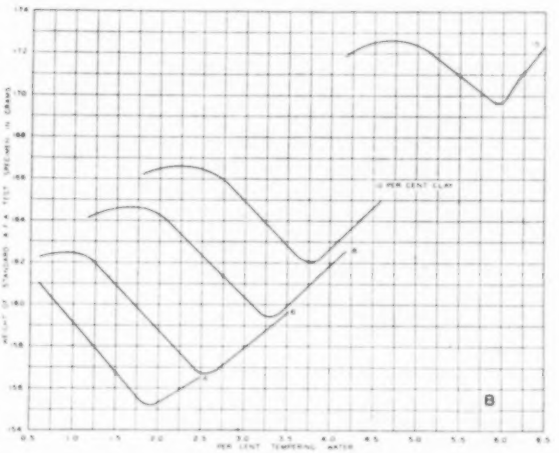

FIG. 4 (*B*).—Sand-clay mixtures containing kaolinite clay showing relation of tempering water to bulk density.

III. Character of Absorbed Water in Relation to Plastic Properties

If the thickness of the water held by the clay minerals in a completely rigid condition is the important factor controlling the bonding strength of clays in molding sands, it would seem that it should also be of importance in controlling other plastic properties of clays. In this connection, the following data and discussion are offered:

Some years ago, a careful study[4] was made on a small laboratory extrusion machine of the relation between the power necessary to extrude various kinds of clay and their water content. In Fig. 6, curves showing some of the results of this work are presented. Curve *A* is for a kaolinite clay, *B* and *C* for clays composed of both kaolinite and illite, and *D*, *E*, and *F*, for clays composed entirely of illite. The outstanding feature of the curves is that with more water than a certain minimum amount, extrusion requires very little power. With water decreasing below this minimum amount, the power necessary to extrude increases

[4] R. E. Grim and R. A. Rowland, unpublished studies made in laboratories of the Illinois State Geological Survey, Urbana, Ill.

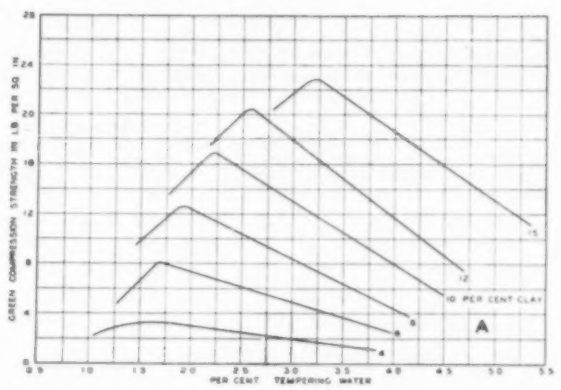

FIG. 5 (*A*).—Sand-clay mixtures containing illite clay showing relation of compression strength to tempering water.

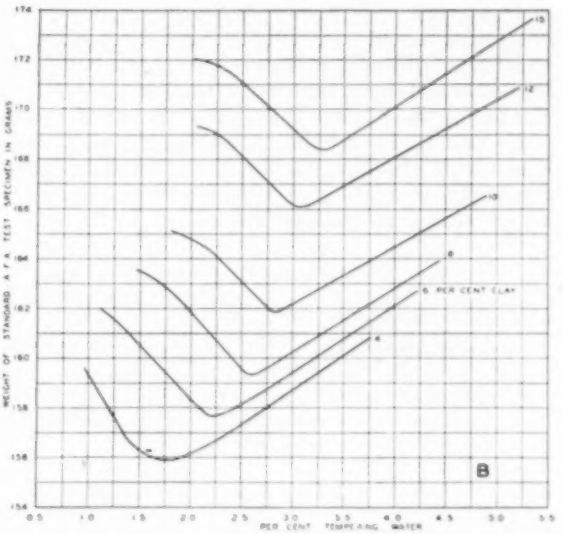

FIG. 5 (*B*).—Sand-clay mixtures containing illite clay showing relation of tempering water to bulk density.

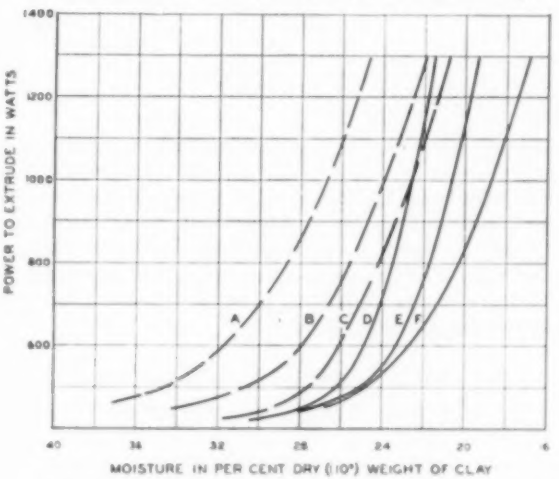

FIG. 6.—Curves showing relation of tempering water in clays and the power necessary to extrude clays through an auger machine.

TABLE III

WATER CONTENT IN PERCENTAGE DRY (100°C.) WEIGHT OF CLAY AT MAXIMUM GREEN COMPRESSION STRENGTH AND MINIMUM BULK DENSITY

Clay in sand-clay mixtures (%)	Illite clay		Kaolinite clay	
	Max. green compression strength	Min. bulk density	Max. green compression strength	Min. bulk density
8	24	32	22	42
10	23	29	22	40
12	22	26		
15	22	23	33	41

rapidly to the point where extrusion is impossible. In other words, there is a very narrow moisture content that marks the transition from easy extrusion to impossible extrusion. An examination of Table III and Fig. 6 shows that maximum green compression strength and minimum bulk density develop for kaolinite and illite clays in the moisture range that is the critical transition range in the extrusion curves. The conclusion seems warranted therefore that in the extrusion of clays, extrusion is about impossible as long as there is no more water than that which will be fixed rigidly by the clay minerals. When the amount of water is increased above this point so that water with incomplete rigidity is present, extrusion becomes easy.

As shown in Table IV, sands bonded with montmorillonite clays and illite clays show no appreciable gain in strength without an accompanying loss of water.

The explanation for air-set strength seems to be that a certain amount of time is required for the water to penetrate some of the basal plane surfaces of the cells of halloysite and kaolinite and to assume fixed positions. Immediately after mixing halloysite-clay-sands with water they have a "wet" feel which disappears within a short time (1 hour ±) without an accompanying loss of water. Montmorillonite-clay-sands show a complete development of strength immediately without air-set strength because water penetrates at once to all available surfaces of montmorillonite. Illite does not break down into individual cells in the presence of water and there is little penetration of water to individual basal surfaces in such clays, and as a consequence there is no air-set strength.

The air-set property shows that for certain clay minerals there is an appreciable amount of time required for water to penetrate to available basal plane surfaces and to become fixed. Under similar conditions for other clay minerals, the penetration is almost instantaneous, and for still others there is no penetration. There is, therefore, a time factor that must be considered in measuring the plastic properties of clays composed of certain clay minerals.

TABLE IV

AIR-SET STRENGTH OF RAMMED SAND-CLAY MIXTURES

Green compression strength determined immediately after ramming (lb./sq. in.)		Compression strength determined the following periods of time after ramming (lb./sq. in.)							
		15 min.		30 min.		1 hr.		3 hr.	
Strength	Moisture	Strength	Moisture	Strength	Moisture	Strength	Moisture	Strength	Moisture
Halloysite clay (12% clay mixture)									
7.0	4.75	14.9	4.45	20.8	4.3	31.5	3.82	51.0	2.45
3.0	5.95	4.0	5.7	5.2	5.4	9.5	5.1	52.5	3.95
Kaolinite clay (10% mixture)									
7.6	3.8	13.2	3.35	17.2	2.95	21.8	2.55	30.0	1.50
4.0	5.2	5.5	4.75	8.0	4.40	13.5	3.7	40.0	1.95
Illite clay (12% clay mixture)									
8.5	4.2	12.2	3.65	15.4	3.37	20.4	2.9	32.3	2.05
5.05	5.4	8.5	4.85	11.6	4.47	17.0	3.95	33.3	2.70
Montmorillonite clay (6% mixture)									
7.75	3.2	9.90	2.85	11.0	2.66	15.8	2.3	27.6	1.70
5.87	4.6	7.0	4.3	8.8	4.0	11.3	3.70	22.8	2.9

Further, it would seem justifiable to suggest that the presence of water with a definite configuration and the point of the beginning of the transition of such water to liquid water are important, perhaps dominant, factors underlying the plastic properties of clays in general. The foregoing data give a first quantitative measure of the transition point in the physical state of the water adsorbed by clays.

IV. Time Factor in Clay-Water Relations

Investigations of the bonding strength of various classes of clays have shown that when rammed specimens of mixtures of sand and halloysite clay or kaolinite clay are allowed to stand in air for short periods of time there is a gradual increase in the bonding strength of the clay without much loss of water (air-set strength).

V. Applications of Suggested Clay-Water Relationships

The clay-water characteristics suggested herein seem to have wide applications in explaining the origin and geologic history as well as the properties of clay materials. Thus, they should help to understand the processes of diagenesis and the difference in the texture between many sediments composed of illite and those composed of kaolinite; sediments composed of the former clay mineral tend to have a laminated texture. They would enter into an understanding of the structures that sometimes develop on a large scale in sediments that are largely unconsolidated.

In the field of ceramics, the range of water contents yielding plastic clay bodies probably corresponds to the water content in excess of that held in a completely

rigid condition and somewhere below the amount where fluid water is abundant. The difficulty in removing water during drying appears to be much greater for oriented rigid water than for fluid water.

In the field of engineering, particularly in soil mechanics, the hitherto puzzling absence of variations of water content with depth encountered in certain soils and clays may find an explanation. Further, it would seem that the clay-water relationship presented herein should explain some of the changes taking place in soils under superimposed load.

VI. Summary

The rigidity of the water held on the surfaces of the clay minerals seems to be a dominant factor determining the bonding and plastic properties of clays. The point of the beginning of the transition of completely rigid water to liquid water is marked by great changes in such properties.

Each type of clay mineral seems to have a characteristic ability to stabilize water, and the exchangeable ions also exert an influence.

In the clay minerals halloysite and kaolinite, the reaction with water is not completed immediately, so that there may be a considerable time lag after mixing the clay and water before certain plastic or bonding properties develop.

The foregoing clay-water characteristics seem to have applications in industry, engineering, and science. Brief illustrations of such applications are given for the fields of geology, ceramics, and soil mechanics.

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University of Illinois Campus
Urbana, Illinois

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GIVING AND RECEIVING ARE COMPLEMENTARY ACTS

There Are No Secrets of Materials and Processes Not Readily Visioned by Competitors

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2. The officers and committeemen ***must*** meet in Hotel Statler, Buffalo, April 16 and 17.

3. Each member in this emergency ***must*** feel it his personal responsibility to continue ceramic research and education through exchange of information.

4. Our Local Sections ***must*** be more active.

5. Our March issue ***must*** carry the titles and abstracts of papers that would have been presented at the Annual Meeting.

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